

**London South Bank**  
University

**Heterogeneous Catalytic Conversion  
of Carbon Dioxide to Value Added  
Chemicals**

**By**  
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of the requirements for the award of Doctor  
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## **DEDICATION**

**This thesis is dedicated to the loving memory of my Mother,**

**Chief (Mrs) Juliana Modupe Adeleye (JP)**

**Though she passed away, I always remember and cherish her  
unflinching commitment to my education and career pursuit.**

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## ABSTRACT

Carbon dioxide (CO<sub>2</sub>) emissions have increased to unsustainable levels in the atmosphere, which has led to the current environmental problems such as climate change and global warming. The reduction of CO<sub>2</sub> emissions has become a global environmental challenge. Greener chemical process for utilisation of CO<sub>2</sub> in the synthesis of valuable chemicals such as organic carbonates is one of technological advancements aimed at reducing CO<sub>2</sub> emission into atmosphere.

Organic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), 4-vinyl-1-cyclohexene carbonate (VCHC), (chloromethyl)ethylene carbonate (CMEC) and styrene carbonate (SC) have been used widely as intermediates in the synthesis of chemicals, pharmaceuticals and fuel additives. The conventional method of organic carbonates syntheses employs homogeneous catalysts, solvents as co-catalysts and toxic raw materials including phosgene (COCl<sub>2</sub>) and *iso*-cyanates (RNCO), and produces carcinogenic by-products that could have serious impact on the environment and human health. Hence, there is a need for an environmentally benign green process for the synthesis of organic carbonate from CO<sub>2</sub>.

Catalysis is an important tool in designing a greener process for the synthesis of valuable chemicals. In this work, several heterogeneous catalysts have been synthesised using a continuous hydrothermal flow synthesis (CHFS) reactor and their catalytic activity evaluated for the synthesis of organic carbonates by cycloaddition reaction of epoxides and CO<sub>2</sub> under a solvent free system. The catalysts were characterised using various analytical characterisation techniques including Raman spectroscopy (RS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS) and x-ray powder diffraction (XRD). The Brunauer-Emmett-Teller (BET)

surface area and porosity measurements were conducted using micrometrics analyser.

Solvent free heterogeneous catalytic process for organic carbonate synthesis has been investigated using a high pressure Parr reactor. The effect of various parameters such as heat-treatment temperature, catalyst loading, CO<sub>2</sub> pressure, reaction time and reaction temperature on the conversion of epoxides, selectivity and yield of organic carbonates was studied for optimisation of reaction conditions. Batch experimental studies were conducted to investigate the long term stability of the catalysts by reusing the catalysts several times for the syntheses of organic carbonates. Ceria, lanthana and zirconia graphene oxide (Ce-La-Zr-GO) nanocomposite catalyst has been the most active and selective for the cycloaddition reaction as compared to other heterogeneous catalysts such as commercially available catalysts (Zr-O, Ce-Zr-O, La-Zr-O and Ce-La-Zr-O catalysts were supplied by the Magnesium Elecktron Limited (MEL) Chemicals) used in this research work. The reusability studies showed that Ce-La-Zr-O and Ce-La-Zr-GO catalysts could be reused several times without losing catalytic activity.

**Keywords:** Carbon dioxide (CO<sub>2</sub>), ceria and lanthana doped zirconia (Ce-La-Zr-O), ceria, lanthana and zirconia graphene oxide (Ce-La-Zr-GO), ceria doped zirconia (Ce-Zr-O), lanthana doped zirconia (La-Zr-O), heterogeneous catalysts, propylene carbonate (PC), propylene oxide (PO), butylene carbonate (BC), butylene oxide (BO), 4-vinyl-1-cyclohexene carbonate (VCHC), 4-vinyl-1-cyclohexene 1,2-epoxide (VCHE), (chloromethyl)ethylene carbonate (CMEC), epichlorohydrin (ECH), catalyst characterization, zirconia (Zr-O).

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## LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BC	butylene carbonate
BO	butylene oxide
CCS	carbon, capture and storage
CMEC	(chloromethyl)ethylene carbonate
CO <sub>2</sub>	carbon dioxide
DMAP	4-dimethylaminopyridine
DMC	dimethyl carbonate
DMF	dimethyl formamide
ECH	epichlorohydrin
EC	ethylene carbonate
EO	ethylene oxide
NGP	natural graphite powder
GO	graphene oxide
h	hour
K	kelvin
<i>n</i>	amount of substance in mole
P <sub>c</sub>	critical pressure
PC	propylene carbonate
PO	propylene oxide
PPN	bis(triphenylphosphine)immium
Py	pyridine
S	selectivity
SC	styrene carbonate
Sc-CO <sub>2</sub>	supercritical carbon dioxide
SO	styrene carbonate
SEM	scanning electron microscopy
SFP	supercritical fluid pump
TBAH	tetrabutyl ammonium halide
TBHP	tert-butylhydroperoxide
T <sub>c</sub>	critical temperature



TEM	transmission electron microscopy
TOF	turnover frequency
VCHC	4-vinyl-1-cyclohexene carbonate
VCHE	4-vinyl-1-cyclohexene 1,2-epoxide
X	conversion
XPS	x-ray photoelectron spectroscopy
XRD	x-ray powder diffraction
Y	yield
°C	degree Celsius
%	percentage

## NOMENCLATURE

$A_c$	area of component
$A_i$	area of internal standard
Al-O	aluminium oxide
AP	as-prepared Ce-La-Zr-GO
AR	area ratio
$C_c$	concentration of component
$C_i$	concentration of internal standard
CR	concentration ratio
Ce-La-Zr-O	ceria and lanthana doped zirconia
Ce-La-Zr-GO	ceria, lanthana and zirconia graphene oxide
Ce-Zr-GO	ceria and zirconia graphene oxide
Ce-Zr-O	ceria doped zirconia
CHFS	continuous hydrothermal flow synthesis
HT-500	as prepared Ce-La-Zr-GO heat-treated at 773 K
HT-700	as prepared Ce-La-Zr-GO heat-treated at 973 K
HT-900	as prepared Ce-La-Zr-GO heat-treated at 1173 K
La-O	lanthanum oxide, lanthana
La-Zr-O	lanthana doped zirconia
Mg-O	magnesium oxide
Zr-O	zirconium oxide, zirconia

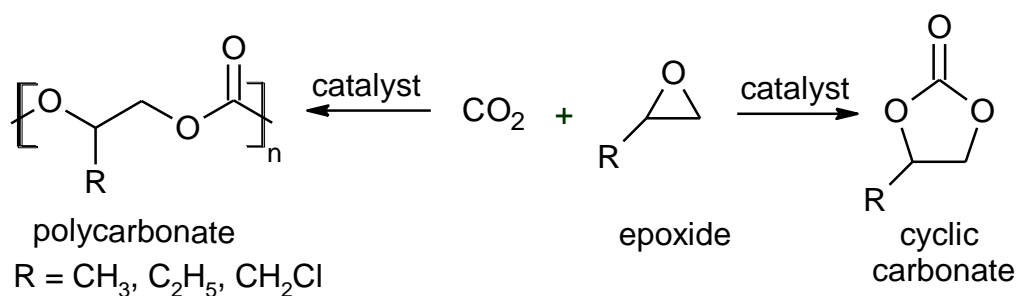
# ***CHAPTER 1***

## ***INTRODUCTION***

## 1. INTRODUCTION

### 1.1. Motivation

Carbon dioxide (CO<sub>2</sub>) is an important raw material for the synthesis of industrially useful chemicals. An application of CO<sub>2</sub> for the chemical synthesis is identified with sustainable chemical industry, which is based on the clean chemical process and reduction of CO<sub>2</sub> emission into the atmosphere (Darensbourg, 2010). Carbon dioxide is one of the primary greenhouse gases, considered as the main factor for current environmental issues such as global warming and climate change (Aresta, 2003). Research efforts have shown that CO<sub>2</sub> is an important compound that could replace the toxic chemicals employed in the conventional syntheses of organic carbonates. The reaction of epoxide and CO<sub>2</sub> to produce organic carbonates (Figure 1.1) is a greener chemical process that is sustainable from both economic and environmental sustainability perspectives. The direction of reaction of the organic carbonates (cyclic carbonates or polycarbonates) syntheses is influenced by the reaction conditions, type of catalysts and nature of the substrates (epoxides).



**Figure 1.1.** Syntheses of polycarbonate and cyclic carbonate from epoxide and CO<sub>2</sub>

Polycarbonates are versatile biodegradable polymeric compounds which are conventionally synthesised using toxic chemicals such as phosgene (COCl<sub>2</sub>) and *iso*-cyanates (RNCO) or hazardous oxidative carbonylation route of carbon monoxide and oxygen. Significant advances in the greener technological processes have been developed for the synthesis of

polycarbonate from the reaction of CO<sub>2</sub> and epoxide, and direct polymerisation of cyclic carbonate (Eghbali and Li, 2007; Ulusoy *et al.*, 2011). These methods have replaced the use of toxic chemicals with renewable, inexpensive, readily available and non-toxic CO<sub>2</sub>. Cyclic carbonates are most preferred organic carbonates from the thermodynamic stability point of view. Cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), (chloromethyl)ethylene carbonate (CMEC), 4-vinyl-1-cyclohexene carbonate (VCHC) and styrene carbonate (SC) are synthesised from the reaction of CO<sub>2</sub> and their corresponding epoxides. Some of these catalytic chemical processes have been commercialised in recent years (North, 2012; Srivastava *et al.*, 2005).

In addition to biodegradability, high solvency and low toxicity, cyclic carbonates possess several unique properties including high boiling and flash point, low odour level and evaporation rate for several organic and inorganic industrially applications. EC, PC and BC have found numerous applications as chemical reactive intermediates (reaction with amines, alcohols, and carboxylic acids) for the preparation of industrially useful compounds such as polymers, surfactant and plasticisers (Clements, 2003; Huntsman Corporation, 2001). In addition, PC and BC are important compounds as cure accelerator reactions such as silicate acceleration used in foundry sand binding and phenol formaldehyde resin extraction used in the manufacture of wood products (Huntsman Corporation, 2008). EC is an excellent reactive intermediate for selective alkoxylation, transesterification, and carbamate formation (Huntsman Corporation, 2001). PC is an important inert solvent in degreasing, paint stripping and cleaning applications (Tomishige *et al.*, 2004; Verevkin *et al.*, 2008). It is used as a chemical intermediate for the production of polycarbonate (Ulusoy *et al.*, 2011), polyurethane (North *et al.*, 2010) and dimethyl carbonate (Cui *et al.*, 2003; Yoshida *et al.*, 2006; Dai *et al.*, 2009). It is also found as a diluent in hydraulic fluid system, lithium battery production

(Machoa *et al.*, 2008) and as a carrier solvent in the production of cosmetic and medication (Clements, 2003). BC is used as a solvent in telomerisation reaction of butadiene and CO<sub>2</sub> for the synthesis of lactone and as a solvent for separation of catalyst from reaction mixture (catalyst containing phase) in hydroformylation reaction (Behr *et al.*, 2005; Behr *et al.*, 2007; Kumelan *et al.*, 2008). BC is an important solvent used in extraction of phenols which are toxic pollutants and their removal from industrial waste streams is very crucial from the health and environmental standpoint (Leopold *et al.*, 2005). VCHC is used as additives, plasticizers, antifoam agent for antifreezing (Lee *et al.*, 2008). CMEC has found an extensive use as agricultural chemicals such as pesticides, insecticides, disinfectants and herbicides (Shaikh and Sivaram, 1996). it is also used as an important intermediate for the production of several chemicals such as hydroxymethyl carbonate (glycerine carbonate), which is used in cosmetics, personal care and medicinal applications (Huntsman corporation, 2010), methoxymethyl carbonate and phenoxymethyl carbonate (Dibenedetto *et al.*, 2011).

Several conventional routes for the syntheses of cyclic carbonates have been identified, which include the phosgenation process, oxidative addition of CO<sub>2</sub> to alkenes (Dibenedetto *et al.*, 2014; Eghbali and Li, 2007), oxidative carboxylation of 1,2-diol/alcohol (Du *et al.*, 2008; Sakakura *et al.*, 2007), and electrochemical processes (North *et al.*, 2010). These conventional synthetic approaches have major drawbacks such as the use of solvents in conjunction with the homogenous catalysts, use of toxic chemicals such as COCl<sub>2</sub> and RNCO, production of large amount of waste chlorinated compounds (hydrochloric acids) and low selectivity to the organic carbonates (Aresta *et al.*, 2003). Therefore, greener routes for the production of cyclic carbonates are highly desirable. As such, cycloaddition of CO<sub>2</sub> and epoxide to produce organic carbonates using suitable solvent free heterogeneous catalysts would be an innovative industrial approach to eliminate the conventional route of cyclic carbonate

synthesis. Solvent free heterogeneous catalytic system is considered as more efficient, economically feasible and greener synthetic route for valuable chemical synthesis. Notably, it offers many advantages over conventional routes including the use of non-hazardous catalysts with increased thermal stability, reusability, elimination of toxic by-products and easy separation of catalyst from reaction mixture (Dai *et al.*, 2009; Adeleye *et al.*, 2014). However, the efficiency of the method is limited by the use of high amount of catalyst and rigorous reaction conditions (Dai *et al.*, 2013).

The catalyst required for organic carbonates syntheses should not only be limited to enhancement of activity and selectivity towards the required organic carbonate products, but also should fulfil the requirement of greener and sustainable chemical process (Pescarmona and Taherimehr 2012). Several heterogeneous catalysts such as metal oxide, zirconia and graphene based metal oxide catalysts were identified, prepared and assessing for their performances in the syntheses of cyclic carbonates.

### 1.2. Research Aims and Objectives

The aims and objectives of the work were to:

- To develop and design a greener and sustainable process for the production of organic carbonates such as propylene carbonate (PC), butylene carbonate (BC), 4-vinyl-1-cyclohexene carbonate (VCHC) and (chloromethyl)ethylene carbonate (CMEC). This was achieved by systematically investigating the suitable procedure for solvent free heterogeneous catalytic processes of cycloaddition reaction of epoxide and CO<sub>2</sub> for organic carbonates syntheses.
- To prepare and investigate the catalytic performance of different heterogeneous catalysts such as metal oxides, zirconia and graphene based nanocomposite inorganic catalysts for the synthesis of organic carbonates. Several heterogenous catalysts

include ceria, lanthana doped zirconia (abbreviated as Ce-La-Zr-O), ceria, lanthana and zirconia graphene oxide (abbreviated as Ce-La-Zr-GO), ceria and zirconia graphene oxide (abbreviated as Ce-Zr-GO), ceria doped zirconia (abbreviated as Ce-Zr-O), graphene oxide (GO), lanthana (labelled as La-O) and zirconia (labelled as Zr-O) were prepared using a continuous hydrothermal flow synthesis (CHFS) reactor. The catalytic activity of the catalysts prepared using hydrothermal processes were compared with the catalysts (Zr-O, Ce-Zr-O, La-Zr-O and Ce-La-Zr-O) supplied by a chemical company (Magnesium Elecktron Limited (MEL) Chemicals). The performances of the catalysts were investigated for the syntheses of organic carbonates from the reaction of epoxides and CO<sub>2</sub>.

- To investigate and compare the reactivity of different epoxides such as propylene oxide (PO), butylene oxide (BO), 4-vinyl-1-cyclohexene epoxide (VCHE) and epichlorohydrin (ECH) for the syntheses of organic carbonates including PC, BC, VCHC and CMEC, respectively. The experimental method included cycloaddition reaction of epoxides and CO<sub>2</sub> to produce corresponding organic carbonates using a high pressure reactor (autoclave reactor) with a solvent free heterogeneous catalyst.
- To characterise different heterogeneous catalysts such as Ce-La-Zr-GO, Ce-La-Zr-O, Ce-Zr-GO, Ce-Zr-O, GO, La-O, La-Zr-O and Zr-O using various analytical characterisation techniques including Raman spectroscopy (RS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRD). The investigation of Brunauer-Emmett-Teller (BET) surface area and porosity measurements are conducted using a micrometrics analyser.

- To investigate the effect of various parameters such as heat-treatment temperature, catalyst loading, CO<sub>2</sub> pressure, reaction time and reaction temperature to determine the optimum reaction conditions for the cycloaddition reaction of epoxides and CO<sub>2</sub> for the production of organic carbonates.
- To investigate the long term stability of the heterogeneous catalysts for the syntheses of organic carbonates. Reusability studies were conducted in a high pressure reactor, the fresh catalyst was reused up to five times for organic carbonate synthesis to investigate the catalyst stability.
- To reduce the process complexity in homogeneous catalytic processes with an effective single step solvent free heterogeneous catalytic process. This was achieved using an effective experimental procedure and reaction mixture/catalyst separation processes.
- To replace the conventional homogeneous catalytic processes with a potentially effective solvent free heterogeneous catalytic system. This was achieved by using of highly stable and inexpensive heterogeneous catalysts.



### 1.3. Organisation of Thesis

Brief description of the chapters in the thesis are summarised as follows:

**Chapter 1: Introduction** – This chapter provides a broad overview of the research work. The motivations and objectives of the research work are clearly highlighted and organisation of the thesis structure is introduced.

**Chapter 2: Literature Review** – The chapter shows an extensive literature review on various methods employed for the conversion of carbon dioxide to organic carbonates, effects of carbon dioxide on global climate, sources of CO<sub>2</sub> as well as importance of CO<sub>2</sub> as a chemical feedstock. The different catalysts used for reaction of epoxides and CO<sub>2</sub> to produce organic carbonate are reviewed. Reactivity of epoxides and the effect of experimental parameters (such as catalyst loading, CO<sub>2</sub> pressure, reaction time and temperature) on the efficiency of organic carbonate synthesis are discussed.

**Chapter 3: Catalyst Preparation and Characterisation** – Chapter 3 describes the preparation of heterogeneous catalysts using continuous hydrothermal flow synthesis (CHFS) process. The instruments and techniques used for characterisations of the catalysts are also explained.

**Chapter 4: Experimental Methods for Cyclic Organic Carbonates Syntheses** – This chapter describes the methodology for the synthesis of organic carbonates from various epoxides and CO<sub>2</sub>. General batch experimental procedure, method of analysis and determination of conversion of epoxides, selectivity and yield of organic carbonates are discussed in details.

**Chapter 5: Heterogeneous Catalysts for Conversion of Carbon Dioxide to Propylene Carbonate (PC)** – This chapter describes batch experimental studies for propylene carbonate synthesis using a high

pressure reactor (autoclave reactor). The effect of various reaction parameters such as heat-treatment temperature, catalyst loading, CO<sub>2</sub> pressure, reaction time, reaction temperature, different catalysts and catalyst reusability studies is also discussed. The method used for the analysis of the samples collected from the reaction mixture is also explained in this chapter.

**Chapter 6: Synthesis of Butylene Carbonate (BC)** – Batch experimental studies for cycloaddition reaction of butylene oxide (BO) and CO<sub>2</sub> to synthesise butylene carbonate (BC) is described in this chapter. The experiments were carried out to optimise the reaction conditions in the presence of ceria, lanthana doped zirconia (abbreviated as Ce-La-Zr-O) and ceria, lanthana and zirconia graphene oxide (abbreviated as HT-500) catalysts. The effect of various reaction parameters such as catalyst loading, CO<sub>2</sub> pressure, reaction time, reaction temperature and catalyst reusability studies on the conversion of BO, selectivity and yield of BC is discussed.

**Chapter 7: Synthesis of 4-vinyl-1-cyclohexene carbonate (VCHC)** – This chapter describes the synthesis of 4-vinyl-1-cyclohexene carbonate (VCHC) from the reaction of 4-vinyl-1-cyclohexene 1,2-epoxide (VCHE) and CO<sub>2</sub>. The experiments were carried out in the presence Ce-La-Zr-O and HT-500 catalysts. The effect of various reaction conditions such as catalyst loading, CO<sub>2</sub> pressure, reaction time, reaction temperature and catalyst reusability studies on the conversion of VCHE, selectivity and yield of VCHC is explained.

**Chapter 8: Synthesis of (chloromethyl)ethylene carbonate (CMC)** – The synthesis of (chloromethyl)ethylene carbonate (CMC) from the reaction of epichlorohydrin (ECH) and CO<sub>2</sub> is described in this chapter. The effect of different experimental parameters on the conversion of ECH,

selectivity and yield of CMEC in the presence Ce-La-Zr-O and HT-500 catalysts is explained.

### **Chapter 9: Conclusion and Recommendations for Future Works –**

Conclusions of the overall research work are summarised and recommendations for the future research work are outlined in this chapter.

**Chapter 10: References** – The bibliographies of all the materials used in this research are outlined in this chapter.

**Chapter 11: Appendices** – Supporting materials that are relevant to the research work are provided in this chapter.

## ***CHAPTER 2***

### ***LITERATURE REVIEW***

## 2. LITERATURE REVIEW

### 2.1. Introduction

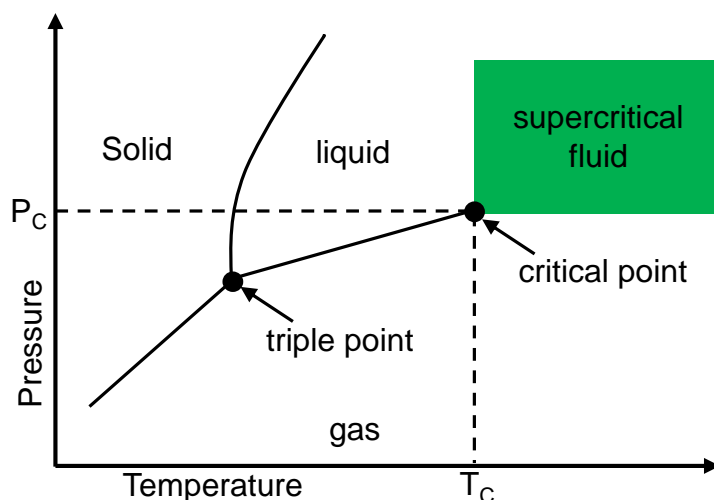
The prerequisite for sustainable environment and green chemical process is the utilisation of renewable raw materials. The readily available renewable carbon source is carbon dioxide (CO<sub>2</sub>) which has the advantages of being non-flammable, nontoxic, abundant, recyclable, chemically inert and economical (Bu *et al.*, 2007; Dai *et al.*, 2009; Paddock and Nguyen 2001). However, CO<sub>2</sub> is a primary greenhouse gas being considered as the major factor responsible for current environmental problems such as global warming and climate change (Aresta, 2003). One of the many attempts aimed at reducing the atmospheric concentrations of carbon dioxide is the utilisation of CO<sub>2</sub> for the synthesis of valuable products such as organic carbonates (polycarbonates and cyclic carbonates). CO<sub>2</sub> is a carbonyl chemical compound that plays an important role in several industrial applications (Aresta *et al.*, 2003; Song and Xiaoping, 2010; Klaus *et al.*, 2011; Song, 2006). The reaction of CO<sub>2</sub> and epoxides to produce cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), styrene carbonate (SC), (chloromethyl)ethylene carbonate (CMEC), vinyl ethylene carbonate (VEC) and 4-vinyl-1-cyclohexene carbonate (VCHC) have gained considerable attention in recent years due to their commercial values and wide industrial applications (Darensbourg, 2007; Wang *et al.*, 2006; Wu *et al.*, 2008).

This chapter summarises the physiochemical properties and applications of CO<sub>2</sub> and organic carbonates (PC, BC, CMEC and VCHC). Reactivity of the substrates (epoxides) and various routes for the syntheses of cyclic carbonates have also been discussed. The syntheses of organic carbonates using homogeneous catalysts and heterogeneous catalysts in the presence of solvents have been reported in numerous research works. However, this chapter focuses on the reaction of epoxides and CO<sub>2</sub> using heterogeneous catalyst in the absence of organic solvents. Furthermore,

the advantages and shortcomings of using heterogeneous and homogeneous catalysts in the syntheses of organic carbonates are highlighted. This chapter also describes the various methods employed in the preparation of heterogeneous catalysts as well as their applications in chemical synthesis.

### **2.2. Physical and Chemical Properties of Carbon Dioxide**

CO<sub>2</sub> is a chemical compound that naturally occurred in the Earth's atmosphere. It is a carbonyl compound composed of two oxygen atoms covalently bonded to a single carbon atom with linear triatomic structure. It is a colourless weak electrophile and soluble in water (Considine, 2005). CO<sub>2</sub> is odourless at low concentrations and at higher concentrations, it has a sharp and acidic odour. CO<sub>2</sub> is 1.5 times heavier than air and has a density of 1.98 kg/m<sup>3</sup> at standard pressure and temperature (Song, 2006). CO<sub>2</sub> has several applications in its gaseous, liquid and supercritical forms. The liquid CO<sub>2</sub> is obtained by compressing CO<sub>2</sub> to 20 bar and then cooled to -18°C, or by compressing the CO<sub>2</sub> to higher pressure at 50.78 bar and temperature of 21°C, and when the pressure reduced to 5.18 bar and -56.6°C temperature, solid CO<sub>2</sub> is formed. The point at which three phases (gas, liquid and solid) of CO<sub>2</sub> co-exist is called triple point. The solid CO<sub>2</sub> (dry ice) can sublime directly into CO<sub>2</sub> gas when absorbed heat without going through the liquid phase. Carbon dioxide attained a single phase at critical conditions of 31°C temperature ( $T_c$ ) and 73 bar pressure ( $P_c$ ) (Patel *et al.*, 2014; Darr and Poliakoff, 1999; Lu *et al.*, 2002;). Supercritical fluid CO<sub>2</sub> is formed at the point above the critical parameters (Figure 2.1).



**Figure 2.1.** A simplified phase diagram of CO<sub>2</sub> illustrating density changes from liquid to gas, where  $P_c$  and  $T_c$  are the critical pressure and temperature, respectively.

### 2.3. Sources and Effects of Carbon Dioxide on Global Climate

CO<sub>2</sub> is a by-product of the metabolic activity of all cells and one of the most important regulators in human body. Song (2006) classified the sources of CO<sub>2</sub> emission as natural, mobile and stationary. The natural source includes human, plants, animals, land earthquake and volcano CO<sub>2</sub> emissions. The stationary and mobile sources include fossil fuel-based electric power plants, manufacturing plants, cars, aircraft, train and ship. Large quantities of commercial CO<sub>2</sub> are generated by various fermentation industry, cement production, ammonia and hydrogen plant (Kroschwitz and Grant, 1993). Recovery of CO<sub>2</sub> from flue gas is another source of commercial CO<sub>2</sub> production. The steps involve in recovery of CO<sub>2</sub> from flue gas include the use of absorbent materials such as ethanolamine, sodium carbonate and potassium carbonate solution, steam heating the absorbent solution to dislodge pure CO<sub>2</sub> followed by compression of the gas into steel cylinder (Considine, 2005). However, the process is economically intensive.

CO<sub>2</sub> is one of the chemical compositions of air. The use of carbon based fossil fuels by human activity through industrial revolution has contributed significantly to an increase in the concentration of CO<sub>2</sub> in the global atmosphere (Houghton *et al.*, 2001). Approximately 80–85% of world source of energy is generated from carbon based fossil fuels (Aresta, 2010) and around 290 billion tonnes of carbon has been emitted to the global atmosphere from fossil fuel and cement production since 1751 (Song, 2006). The continuous CO<sub>2</sub> emission and accumulation in the atmosphere has been a major concern. It has been reported that the atmospheric concentration of CO<sub>2</sub> has increased from 278 ppm in pre-industrial era to ~403 ppm in May 2015 which is far above the safe limit of 350 ppm (Aresta, 2010; IPCC, 2014; NOAA/ESRL, 2015). Ecological system depends on CO<sub>2</sub> as a source of carbon in plant photosynthesis and food production in autotrophic bacterial such as heterotrophic and pathogenic bacteria (Considine, 2005). The emission of greenhouse gases particularly CO<sub>2</sub> into the global atmosphere has inevitably induced rising in temperature, water level and change solid surface of the earth (Houghton *et al.*, 2001). The reduction of wildlife such as polar bear is a significant evidence of the effect of increase in CO<sub>2</sub> concentration in the atmosphere (Boutin, 2010). Other effects of climate change identified with accumulation of CO<sub>2</sub> in the atmosphere include global warming, extreme low global temperature/snow, ash cloud, ocean acidification and acid rain (Song, 2006).

Strategies to reduce the emission of CO<sub>2</sub> will require the combination of innovative ideas and revolutionary approaches, which include the use of green energy sources as alternative to the existing energy system. For example, use of natural gas to replace coal, and the use of renewable energy such as hydropower, solar energy, wind energy, and biomass are important technological innovatives for minimising the emission of CO<sub>2</sub>. Limitation of biomass and animal waste as a fuel energy includes regional and seasonal availability, energy density and demand (Considine, 2005).



The efficiency of catalytic process for CO<sub>2</sub> utilisation to produce useful higher molecular mass hydrocarbons such as organic carbonates is an important greener technological approach to reduce the emission of CO<sub>2</sub>. However, recent studies showed that the rate at which CO<sub>2</sub> accumulate in the global atmosphere through the use of carbon based fossil fuel by human activities is higher compared to amount of CO<sub>2</sub> consumed in the production of valuable chemicals, organic materials and fuels (Klaus *et al.*, 2011). As such, achieving balance between the CO<sub>2</sub> utilisation and emission is a major challenge.

### 2.4. Carbon Dioxide Utilisation

Greener chemical process of CO<sub>2</sub> utilisation is an innovative system aiming to replace the conventional process of producing industrially important chemicals. The approach contributes to the reduction of CO<sub>2</sub> emission into the atmosphere, substitutes the use of carcinogenic raw materials such as phosgene, *iso*-cyanate, carbon monoxide (CO) and chlorofluorocarbons (CFC) as well as congeners, which possess a climate change power (CCP). Arakawa *et al.* (2001) & Aresta and Dibenedetto (2007) reported that approximately 110 Mega tonnes (MT) of CO<sub>2</sub> are currently consumed annually in the chemical syntheses including the commercial process of urea, salicylic acid, cyclic carbonate, polycarbonates, methanol and inorganic carbonates. The urea synthesis consumed largest amount of CO<sub>2</sub> and considered as an active form of CO<sub>2</sub>. Around 146 Million tonnes (Mt) of CO<sub>2</sub> is consumed in urea synthesis and 46 Mt of CO<sub>2</sub> is used in inorganic carbonate (mostly Na<sub>2</sub>CO<sub>3</sub> through solvay process) production in 2008. About 6 Mt/y of methanol and 60 killo tonnes (kt) of CO<sub>2</sub> have been used in salicylic acid production in 2003 (Kember *et al.*, 2011). It is noteworthy that salicylic acid and urea syntheses require no catalysts. Typically 18 Mt/y of CO<sub>2</sub> are used as a supercritical fluid. One of the major successive processes of CO<sub>2</sub> utilisation is in cyclic carbonate and polycarbonate syntheses.

Approximately 18 Mt/y of CO<sub>2</sub> is consumed in polycarbonate and cyclic carbonate syntheses (Song, 2006).

Aresta (2003) stated that about 13.5 Mt/y of CO<sub>2</sub> are consumed in technological use such as food processing, carbonated beverages, metal fabrication, agriculture, nuclear power station, chemical processing, plastic and rubber manufacturing. In addition, CO<sub>2</sub> is used as a mild oxidant or selective source of oxygen atom in chemical industry. Dissociation of CO<sub>2</sub> on the heterogeneous catalysts surface produces active oxygen species. Rao *et al.* (2009), Reddy *et al.* (2009) and de Moraes Batista *et al.* (2010) investigated the utilisation of CO<sub>2</sub> for dehydrogenation of ethyl benzene to produce styrene over the composite mixed metal oxide. Song (2006) and Chen *et al.* (2010) reported dehydrogenation of low alkanes to produce alkyne (ethane, propane and butane to produce ethylene, propylene and butylene respectively). As such, CO<sub>2</sub> is typically not a toxic substance under controlled condition. It is also considered as a safe reagent or solvent, particularly when supercritical CO<sub>2</sub> is used as a process reaction medium (Aresta, 2010).

### **2.4.1. Supercritical Carbon Dioxide (scCO<sub>2</sub>) as an Important Chemical Reaction Medium**

The syntheses of inorganic and organic compounds have been investigated using supercritical CO<sub>2</sub> as a solvent or reaction medium or co-reactant (Yasuda *et al.*, 2002; Kawanami *et al.*, 2003; Lu *et al.*, 2004; Darensbourg and Fitch, 2009). Utilisation of CO<sub>2</sub> in its liquid or supercritical form is an innovative approach aiming to replace traditional solvent in valuable chemical synthesis. The advantages of using supercritical CO<sub>2</sub> for organic carbonate synthesis include reduced heat and mass transfer resistance, avoidance of coke formation and catalyst poisoning, ease product separation, improved conversion and selectivity for inorganic and organic synthesis (Baiker, 1999; Du *et al.*, 2005; Wang *et al.*, 2006). The industrial applications of supercritical CO<sub>2</sub> include utilisation

in laundry cleaning, water treatment, as solvent in polymerisation, cleaning of electronic and antibacterial compounds (Aresta, 2010; Song, 2006). In addition, supercritical CO<sub>2</sub> is advantageous over traditional organic solvent in extraction processes. It allows contaminant-free extraction processes in beverages (caffeine from coffee bean), foods (excess oil from fried potato chips), organic and inorganic functional materials (oils and waxes to herb and pharmaceutical) (Beckman, 2004; Considine, 2005; Kemmere and Meyer, 2005). It is also used to remove pollutant such as polycyclic aromatic hydrocarbons (PAHs) from waste sludge and contaminated soils (Song, 2006).

### **2.4.2. Industrial Applications of Carbon Dioxide**

CO<sub>2</sub> is not just a waste product generated from combustion of organic compound and a primary greenhouse gas for the current environmental issues; it is an important renewable raw material for the synthesis of several valuable chemicals, fuels and carbohydrates (food). Utilisation of CO<sub>2</sub> as a feedstock for the production of organic carbonates continues to receive attention in recent years (Darensbourg and Holtcamp, 1996; Omae, 2006). Highly versatile nature of CO<sub>2</sub> has been exploited in various industrial applications such as chemicals, pharmaceuticals, foodstuffs, beverage, healthcare, environment, pulp and paper, electronics, metals industry, laboratory and analysis, and safety (Kroschwitz and Grant, 1993). However, thermodynamic stability of CO<sub>2</sub> has limited the wider utilisation as a reagent for chemical synthesis (He *et al.*, 2009; Miao *et al.*, 2008).

CO<sub>2</sub> is an essential chemical raw material in greener synthesis of inorganic and organic chemicals, pharmaceuticals and pharmaceutical intermediates (carboxylic acid), urea (for making fertiliser), esters, salicylic acid, aspirin, cyclic carbonates, polycarbonates, dimethyl carbonate (Bai *et al.*, 2011; Centi *et al.*, 2013; Dai *et al.*, 2009; Dibenedetto *et al.*, 2013). It is an important ingredient in beverage and food industries such as in

carbonation of soft drink, mineral water and beer, and drinking water treatment (Song, 2006). Liquid CO<sub>2</sub> is used as a cryogenic fluid in chilling or freezing operations and dry ice (solid) CO<sub>2</sub> is use for temperature control during storage and distribution of foodstuffs. CO<sub>2</sub> is an essential chemical in foodstuffs packaging due to its inert properties and inhibiting effect on micro-organisms (Considine, 2005). CO<sub>2</sub> is typically used as an alternative to electrical stunning in animal processing for food. CO<sub>2</sub> is not just a by-product of the metabolic activity of all cells, but it is an essential chemical for healthcare sector. It is also used to regulate human body activity such as human organs, blood vessel and the respiratory system (Considine, 2005).

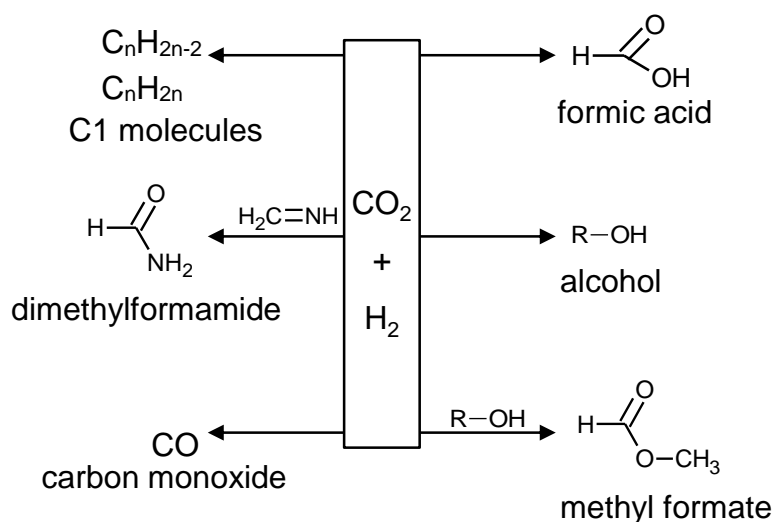
Environmental sector and metal industry used CO<sub>2</sub> as a neutralising agent for controlling pH balance of waste water treatment and liquid effluents. Moreover, precipitate of calcium carbonate produced from reaction of CO<sub>2</sub> and CaO is typically an active ingredient in paper industry as a whitener. CO<sub>2</sub> is usually used as an inert solvent such as fire extinguisher (Song, 2006). One of the most promising applications of CO<sub>2</sub> is its utilisation in the synthesis of valuable chemicals with high economic, health and environmental benefits (Arakawa *et al.*, 2001).

### **2.4.3. Value Added Chemicals Produced from Carbon Dioxide**

Utilisation of CO<sub>2</sub> as a chemical feedstock may not be able to compensate emission of CO<sub>2</sub> into atmosphere. However, the innovative approach of CO<sub>2</sub> utilisation as non-toxic, renewable and low cost carbon source potentially provides access to wide varieties of valuable chemicals (Pescarmona and Taherimehr, 2012). The industrial utilisation of CO<sub>2</sub> includes large scale production of hydrogenation products, carboxylic acid, urea, urethanes, salicylic acid, esters, lactones and numerous carbon based products. In addition to industrial application of CO<sub>2</sub>, production of biodegradable thermoplastic organic carbonates such as polycarbonates and cyclic carbonates (Omae, 2006; Klaus *et al.*, 2011).

### 2.4.3.1. Hydrogenation Products

CO<sub>2</sub> hydrogenation products include carbon monoxide, carboxylic acid, methyl alcohol, methyl formate, and dimethyl formamide. Figure 2.2 shows the reaction schemes for the synthesis of various chemicals using CO<sub>2</sub>. CO<sub>2</sub> hydrogenation is the reaction of CO<sub>2</sub> and hydrogen with or without catalyst. Homogeneous catalysts such as transition metal complexes and ionic liquids are frequently used for CO<sub>2</sub> hydrogenation reaction with relatively good yield (Centi *et al.*, 2013). The limitation of this reaction include production of large amount of by-products, expensive catalyst separation and product purification processes, low conversion and selectivity, and high input of energy (Omae, 2006; Sakakura *et al.*, 2007). Methanol formation is one of the major reactions in CO<sub>2</sub> hydrogenation. Methanol finds application in chemical industry, as a fuel additive (methyl-tertiary-butyl ether, MTBE) and in transesterification of vegetable oil (Centi and Perathoner 2009).

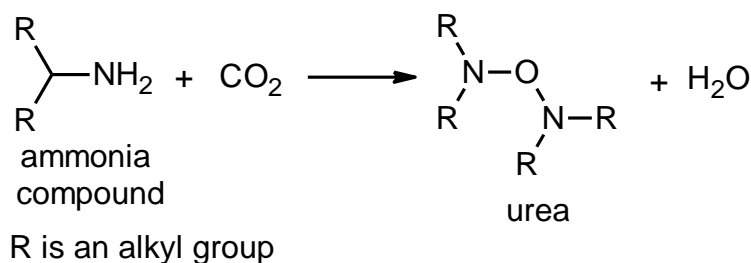


R is an alkyl group

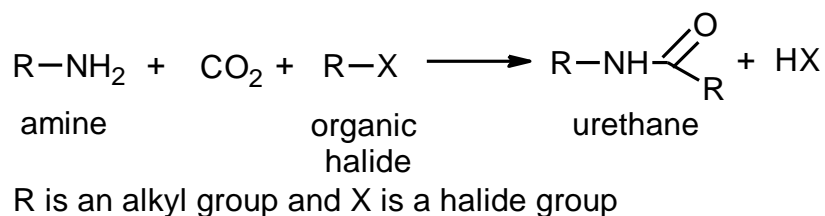
**Figure 2.2.** Hydrogenation reaction of CO<sub>2</sub>

### 2.4.3.2. Synthesis of Urea and Urethanes

Urea (carbamic acid ester) and urethanes (carbamates) are valuable chemicals with several industrial applications. Urea found utility as chemical intermediate in production of fertilizer, urea resin, urea melamine resin, organic chemicals and as additives in animal feed (Ceresana, 2012). Urethane is an important precursor of pharmaceutical products and agricultural chemicals (herbicides, fungicides and pesticide) (Bluestein, 1981; Kreye *et al.*, 2013). Urea is commercially produced by the reaction of CO<sub>2</sub> and ammonia organic compounds as shown in Figure 2.3. Urethanes are synthesised *via* the reaction of CO<sub>2</sub> and amine in the presence of organic compounds such as organic halides, alcohol, organic carbonates, acetylenes, olefin, epoxides, and organometallic compounds (Figure 2.4). Several heterogeneous and homogeneous catalysts such as mesoporous silica containing ammonium salts and adenine-modified Ti-incorporated mesoporous silica have been studied for the synthesis urethane (Sakakura *et al.*, 2007; Kreye *et al.*, 2013).



**Figure 2.3.** Synthesis of urea from reaction of ammonium organic compound CO<sub>2</sub>.



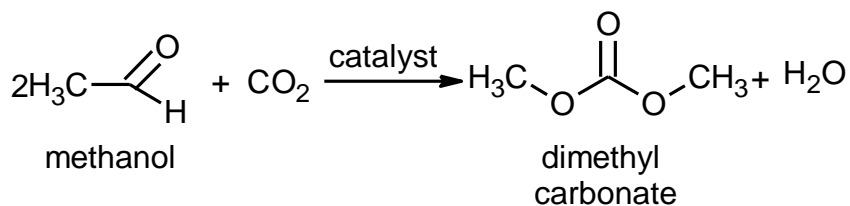
**Figure 2.4.** Synthesis of urethane from reaction of amine and CO<sub>2</sub>.

#### 2.4.3.3. Synthesis of Esters and Lactones

Esters are synthesised *via* the reaction of CO<sub>2</sub> and carbon – carbon unsaturated compound in the presence of palladium catalyst. Lactones are produced from the reaction of CO<sub>2</sub> and unsaturated compounds such as alkynes (acetylene), conjugated diene (1,3-butadiene), diynes (diacetylene) and benzene in the presence of transition metal compounds as catalysts (Sakakura *et al.*, 2007).

#### 2.4.3.4. Syntheses of Acyclic Carbonates

Acyclic carbonate such as dimethyl carbonate (DMC) is one of the valuable chemical compounds that is produced commercially (Bian *et al.*, 2009; Bansode, 2014). DMC finds applications as a solvent, an octane booster in gasoline to meet oxygenate specification and a starting material in organic synthesis (Srinivas *et al.*, 2004; Dai *et al.*, 2009). Several routes of DMC synthesis have been reported including phosgene and methanol process, transesterification of cyclic carbonate and methanol, oxidative carbonylation of methanol and carbon monoxide, and methyl nitrite (Machoa *et al.*, 2008; Sakakura and Kohno, 2009). The synthesis of dimethyl carbonate through oxidative carbonylation or phosgenation of methanol is considered not safe due to production of toxic by-products such as chlorine, phosgene, and carbon monoxide (Bhanage *et al.*, 2003). Synthesis of DMC *via* the reaction of CO<sub>2</sub> and methanol (Figure 2.5) in the presence of heterogeneous catalysts (Yoshida *et al.*, 2006; Ma *et al.*, 2009) has attracted an increasing interest due to the safe reaction procedure and the use of non-toxic and renewable carbon source CO<sub>2</sub> (Beckman, 2004; Centi *et al.*, 2013; Dibenedetto *et al.* 2014). Bhanage *et al.* (2003) reported two step reactions of synthesis for the DMC which involves the reaction of CO<sub>2</sub> and epoxides (ethylene oxide and propylene oxide) to produce cyclic carbonate, followed by the reaction of cyclic carbonate and methanol to produce dimethyl carbonate in the presence of magnesium oxide (MgO) catalyst.

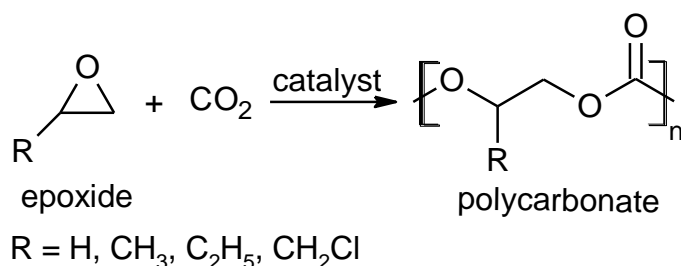


**Figure 2.5.** Synthesis of dimethyl carbonate from reaction of methanol and CO<sub>2</sub>.

#### 2.4.3.5. Syntheses of Polycarbonates

Polycarbonates also known as polymeric compound or linear organic carbonate is an example of organic carbonates that represent various types of polymers with different physiochemical properties. Polycarbonate can be defined as polymer containing carbonate groups (-O-(C=O)-O-). Polycarbonates such as poly-propylene carbonate (PPC), poly-cyclohexene carbonate (PCHC), poly-ethylene carbonate (PEC) and poly-butylene carbonate (PBC) have been commercially produced on a large scale (Pescarmona and Taherimehr, 2012). Copolymerisation reaction of CO<sub>2</sub> and epoxide in the presence of suitable catalysts produce polycarbonates as shown in Figure 2.6. Many catalysts have been investigated for the synthesis of polycarbonate *via* copolymerisation of CO<sub>2</sub> and epoxide, catalysts such as chiral cobalt complexes and organic salts (Coates and Jeske, 2009; Ren *et al.*, 2009) and salen metal complex (Darensbourg, 2007; Pescarmona and Taherimehr, 2012). The concept of copolymerisation reaction of CO<sub>2</sub> and epoxides include the potential possible replacement of traditional environmentally malign industrial processes involving polycondensation reaction of trans-diols and phosgene to produce poly(oxycarbonyloxy-1,4-phenylene) or isopropylidene-1,4-phenylene (Bisphenol-A) (Darensbourg *et al.*, 2003; Klaus *et al.*, 2011).



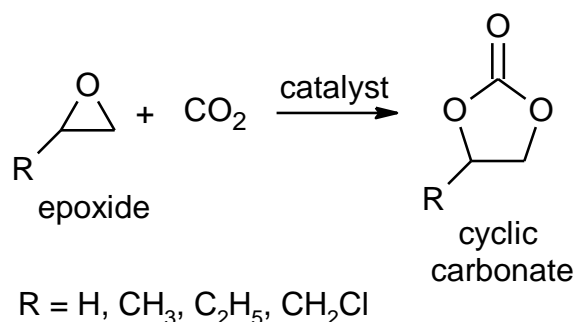


**Figure 2.6.** Synthesis of polycarbonate by reaction of epoxide and CO<sub>2</sub>.

In addition to excellent physico-mechanical properties due to high molecular weight, polycarbonates possess high strength, lightness, durability, biodegradability, heat resistance, transparency and good electrical insulation. The industrial applications of polycarbonate include glass and metal substitute (glazing and sheeting), material for data storage such as CDs and DVDs, electronic components, optical lenses, construction materials, automotive, aircraft components, engineering plastic elastomer, packaging materials, binders, adhesives and coatings. However, low thermal stability and easy thermal deformation limit of the polycarbonates applications (Lee *et al.*, 2012; Pescarmona and Taherimehr 2012). Therefore, polycarbonates syntheses from epoxide and CO<sub>2</sub> has suffered the tendency of cycloaddition reaction which thermodynamically favours the synthesis of five-membered ring cyclic carbonates (Darensbourg *et al.*, 2008).

#### 2.4.3.6. Syntheses of Cyclic Carbonates

Cyclic organic carbonates are industrially important chemicals with several established and potential applications. Cycloaddition reaction of epoxide and CO<sub>2</sub> in the presence of suitable catalysts produces cyclic carbonates (see Figure 2.7). Syntheses of cyclic carbonates from the reaction of epoxide and CO<sub>2</sub> have attracted much interest due to atom efficiency of the process as there is no formation of side products. It also provides a greener alternative to the conventional process, which employed the use of toxic chemicals as a starting material (Han *et al.*, 2011; Dibenedetto *et al.*, 2013).



**Figure 2.7.** Syntheses of cyclic carbonates by cycloaddition of epoxide and CO<sub>2</sub>.

The reaction of epoxide and CO<sub>2</sub> produces two major products (polycarbonates or cyclic carbonates) and side products. The selectivity for polycarbonates or cyclic carbonates generally depends on the catalysts, substrates (epoxides) and reaction conditions.

### 2.5. Applications and Physicochemical Properties of Cyclic Carbonates

Physicochemical properties of the cyclic carbonates synthesised from the reaction of epoxide and CO<sub>2</sub> are strongly influenced by the nature of the catalysts and substrates (epoxides). In addition to biodegradability, high solvency, low toxicity and volatility, cyclic carbonates possess several unique properties such as high boiling and flash point, high relative density, low odour level and evaporation rate. Table 2.1 shows the properties of some industrially important cyclic organic carbonates such as BC, CMEC, EC, PC, SC and VCHC. Consequently, cyclic carbonates are considered as safe chemical solvents for several organic and inorganic industrial applications (Tomishige *et al.*, 2004). Cyclic carbonates are colourless liquid, nearly insoluble in water. They are soluble in many organic solvents, particularly polar solvents including esters, alcohols, ketones, ethers, and aromatic hydrocarbons (Shaikh and Sivaram, 1996). Propylene carbonate is soluble in water at 25 g of PC to 100 g of water and in organic solvents such as polyethylene oxide and other polymer electrolyte.


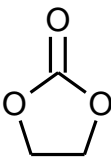
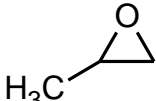
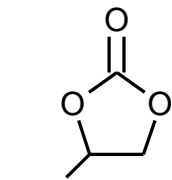
**Table 2.1.** Properties of industrially important cyclic organic carbonates.

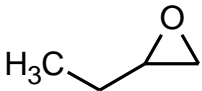
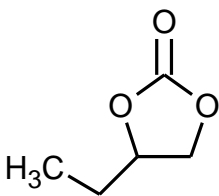
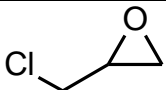
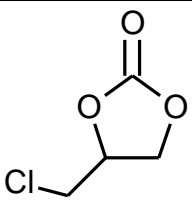
<b>Organic carbonates</b>						
<b>Properties</b>	<b>BC</b>	<b>CMEC</b>	<b>EC</b>	<b>PC</b>	<b>SC</b>	<b>VCHC</b>
Molecular weight (g/mol)	116.12	136.54	88.06	102.09	164.15	168.32
Density (g/mL) at 25°C	1.141	1.369	1.321	1.189	1.25	1.312
Boiling point (°C)	250	314.77	248	240	354.8	284
Melting point (°C)	-45	-	36.4	-55	-	-
Freezing point (°C)	50	-	36	-49	-	-
Flash point (°C)	135	162.74	143	135	171.1	-

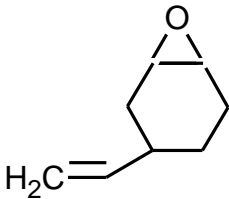
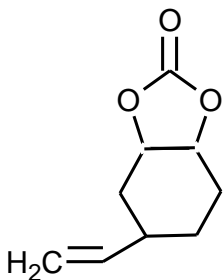
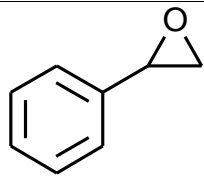
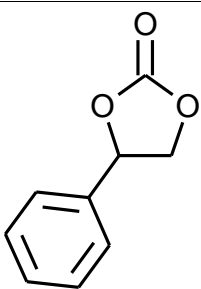
Due to wider applications and high demand of cyclic carbonates as chemical intermediate for valuable chemical synthesis, utilisation of non-toxic, readily available, cheap and renewable CO<sub>2</sub> as a feed stock for their synthesis has been studied extensively. Production of cyclic carbonates from epoxides and CO<sub>2</sub> in the presence of potassium iodide (KI) as a catalyst has been commercially produced since 1950s (Dai *et al.*, 2009; Ion *et al.*, 2009). Cyclic carbonates find application as environmentally friendly organic solvents, intermediates for polycarbonates, polyurethanes, DMC, an electrolyte for lithium ion batteries and as fuel additives (Fujita *et al.*, 2002; Srinivas *et al.*, 2004; Du *et al.*, 2005; Sakakura *et al.*, 2007; Schaeffner *et al.*, 2010). Several catalysts have been investigated for the syntheses of cyclic carbonates. The methods of preparation of cyclic carbonates, the effects of substrates (epoxides) and reaction conditions for cyclic carbonates syntheses are discussed in detail in the following

sections. Table 2.2 shows the applications of most employed industrially important cyclic carbonates.

**Table 2.2.** Application of some industrially important cyclic carbonates.

Starting material	Cyclic carbonate	Applications	References
 Ethylene oxide (EO)	 Ethylene Carbonate (EC)	Chemical intermediate in the production of polycarbonates and dimethyl carbonate. Used as reactive diluent in urethane and epoxy resin syntheses. Solvent in textile dye, surface coating, antipilling, and plasticizer applications. Reactive intermediate in wood binder resin and foundry sand binders production.	Huntsman, 2008a; Tomishige <i>et al.</i> , 2004.
 Propylene oxide (PO)	 Propylene carbonate	Chemical intermediate in the production of polycarbonates and polyurethanes. Solvent in degreasing, paint	Shaikh and Sivaram 1996; Clements, 2003; Tomishige <i>et al.</i> , 2004;

	(PC)	stripping and cleaning applications. Used as a diluent in hydraulic fluid system and lithium battery production. Carrier solvent in the production of cosmetic and medication.	Verevkin <i>et al.</i> , 2008.
 <chem>CCCC1OC1</chem> Butylene oxide (BO)	 <chem>CCCC1OC(=O)OC1</chem> Butylene carbonate (BC)	Used as a diluent in hydraulic fluid system and lithium battery production. Solvent in catalyst preparation and telomerisation reaction. Accelerant in dye, printing, foundry sand and wood binding applications, Used as a phenol extraction.	Chung <i>et al.</i> , 1999; Clements, 2003; Leopold <i>et al.</i> , 2005; Behr <i>et al.</i> , 2005; Behr <i>et al.</i> , 2007; Huntsman, 2008b.
 <chem>ClCC1OC1</chem> Epichlorohydrin (ECH)	 <chem>ClCC1OC(=O)OC1</chem> (chloromethyl) ethylene carbonate (CMEC)	Used in the production of agricultural chemicals such as pesticides, fungicides and pesticide Reactive Intermediate for various chemicals	Shaikh and Sivaram 1996; Huntsman, 2010; Chemsink .com; Gomez <i>et</i>

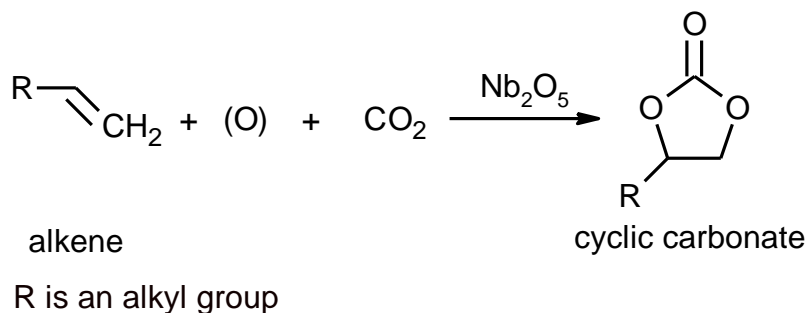
		such as glycerine carbonate, phenylmethoxymethyl carbonate, methoxymethyl carbonate. Used in the production of cosmetics, personal care and medicine	<i>al.</i> , 2012.
 <p>4-vinyl-1-cyclohexene 1,2-epoxide (VCHE)</p>	 <p>4-vinyl-1-cyclohexene carbonate (VCHC)</p>	Antifoam agent for antifreezing. Used as a plasticizers. Chemical intermediate in the production of polycarbonates.	Lee <i>et al.</i> , 2008.
 <p>Styrene oxide (SO)</p>	 <p>Styrene carbonate (SC)</p>	Electrolyte in lithium secondary batteries. Precursor for various chemicals i.e. polycarbonates.	Dibenedetto <i>et al.</i> , 2013.

## 2.6. Methods for Cyclic Organic Carbonates Syntheses

Several routes have been reported for the syntheses of organic cyclic carbonates. The current methods include oxidative carboxylation of alkenes, phosgenation reaction, and cycloaddition of epoxides and CO<sub>2</sub>. These methods are briefly described; however, the cyclic carbonates syntheses through cycloaddition reaction of epoxides and CO<sub>2</sub> is described in more detail in the following section.

### 2.6.1. Oxidative Carboxylation of Alkenes

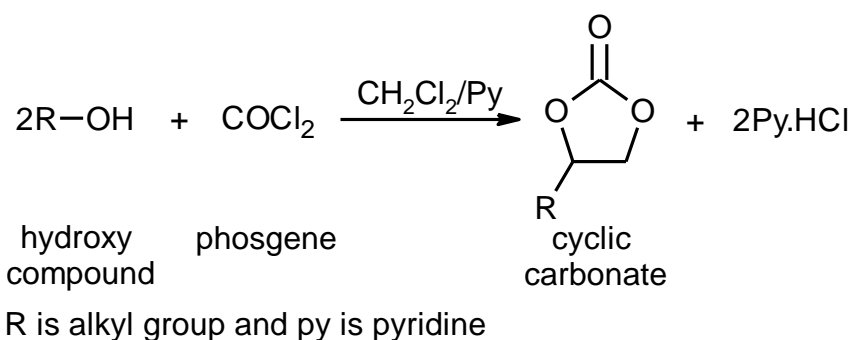
Inexpensive and simple method of cyclic carbonates syntheses would have been direct incorporation of CO<sub>2</sub> into the alkenes in the presence of molecular oxygen i.e. oxidative carboxylation of alkenes. The process has been known since 1962 (Eghbali and Li, 2007). The reaction was carried out as a one-pot reaction or by two consecutive reaction steps. Performing the reaction with a single-step route (one-pot reaction) would be safer and involve lower costs, as would not require purification and handling of epoxides. On the other hand, the two steps reaction would require a multifunctional catalysts that is capable of catalysing the oxidation of alkenes to epoxides, which is known as epoxidation process (Mohammed *et al.*, 2013), followed by the reaction of epoxides and CO<sub>2</sub> to produce cyclic carbonates. The major shortcoming of the reaction is the development of suitable catalyst and process technology. Few suitable catalysts have been developed for the direct syntheses of carbonates from alkenes, which include niobium oxide (Nb<sub>2</sub>O<sub>5</sub>) (Sakakura *et al.*, 2007) and bromine hydrogen peroxide in water (Eghbali and Li, 2007). Figure 2.8 shows direct synthesis of cyclic carbonate from the oxidative carboxylation of alkene. As such, several cyclic carbonates can be synthesised through this method. However, the method received less attention due to low yield and selectivity of the desired product, expensive catalysts and oxidizing reagents employed, and formation of several oxidative by-products (Sun *et al.*, 2005).



**Figure 2.8.** Oxidative carboxylation of alkenes.

### 2.6.2. Phosgenation Reaction

Phosgenation is the traditional method of cyclic carbonate synthesis *via* the reaction of phosgene and 1,2-diol in the presence of organic halides and pyridine as catalysts (Shaikh and Sivaram, 1996; Aresta *et al.*, 2003) as shown in Figure 2.9. Disadvantages of the process include the use of toxic phosgene as a starting material, low yield and selectivity of cyclic carbonate, complex separation process and production of hazardous waste hydrochloric acid (Aresta *et al.*, 2003).



**Figure 2.9.** Phosgenation reaction of cyclic carbonate synthesis.

### 2.6.3. Carboxylation of 1,2-diols

Reaction of 1,2-diols such as propylene glycol and phenyl glycol and  $\text{CO}_2$  to produce corresponding cyclic carbonate is shown in Figure 2.10. the efficiency of several catalysts which include solid supported copper iodide (North *et al.*, 2010), palladium (Pd) (Sakakura *et al.*, 2007), magnesium (Mg) and magnesium oxide (MgO) (Du *et al.*, 2008) have been

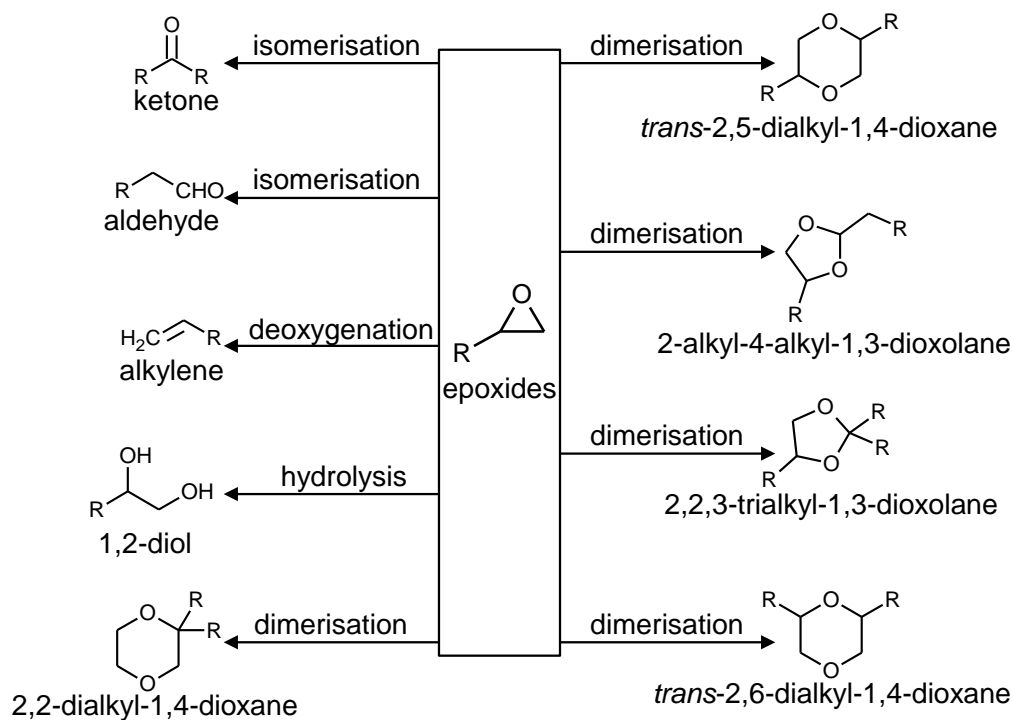




Carboxylation of epoxide to produce cyclic carbonate represents an



Carboxylative syntheses of cyclic carbonates have attracted much interest in terms of atom efficiency and environmental benefits (Shibata *et al.*, 2011). The main side products associated with cycloaddition reaction of CO<sub>2</sub> and epoxides include the dimers of epoxides and their derivatives such as 2,2-dialkyl-1,4-dioxane, trans-2,5-dialkyl-1,4-dioxane, trans-2,6-dialkyl-1,4-dioxane, 2-alkyl-4-alkyl-1,3-dioxolane and 2,2,3-trialkyl-1,3-dioxolane as well as isomers of epoxides including ketones and aldehydes, and hydrolysis of epoxides such as 1,2-diol (Fasi *et al.*, 2001; Aresta and Dibenedetto, 2002; Du *et al.*, 2005; Wang *et al.*, 2007; Ion *et al.*, 2009; Adeleye *et al.*, 2014). Figure 2.12 shows the possible side products and transformation pathways of epoxides in a confined environment such as autoclave reactor. Generally, cycloaddition reaction between inert CO<sub>2</sub> and high energy starting material epoxides is exothermic (Dai *et al.*, 2010; Whiteoak *et al.*, 2012; Yasuda *et al.*, 2006) and requires a suitable catalyst with high energy substrate to achieve desirable conversion of epoxide and selectivity of cyclic carbonates.

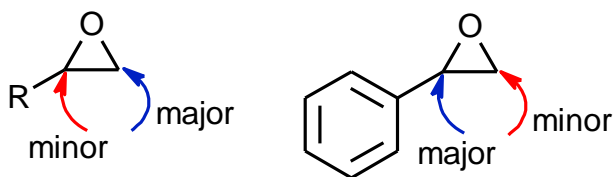


R is an alkyl group

**Figure 2.12.** Possible side products and transformation pathways of epoxides.

### **2.7. Activity of Substrates (Epoxides) and Reaction Conditions for Cyclic Carbonates Syntheses**

Reaction rate and efficiency of the cyclic carbonates syntheses do not depend only on the catalytic system, but it is also influenced by the nature of the substrates and experimental parameters such as type and amount of catalyst, amount and form of CO<sub>2</sub> pressure (gas and supercritical), reaction time and temperature, and mass transfer resistance. Nature of attached groups on the epoxides has been an influence on the activity of epoxide to produce organic carbonates. Position and accessibility of carbon atom, and form of electronic effect of the attached group on the epoxides affect the rate of cycloaddition reaction with CO<sub>2</sub> to produce cyclic carbonates. Styrene oxide (SO) has a high tendency to produce cyclic carbonate rather than polycarbonate as compared to aliphatic terminal and internal epoxides such as propylene oxide (PO) and cyclohexene oxide (CHO) due to the position at which the epoxide is attacked by a nucleophile (an electron donating specie). Figure 2.13 show the most likely position of the epoxide to be attacked during cycloaddition reaction. Wu *et al.* (2010) investigated the reactivity of epoxides and CO<sub>2</sub> to produce organic carbonates. It was found that less steric congested carbon atom on the epoxide is more likely to attack, leading to ring opening of epoxide as compared to epoxides with high number of the attached linear alkyl group (high steric congestion). Epoxide with electron withdrawing group (such as phenyl group in styrene oxide) has higher tendency to produce cyclic carbonate as compared to epoxide with electron donating groups (terminal epoxides). Similarly, epichlorohydrin (ECH) with electron withdrawing chloromethyl group show higher tendency of producing cyclic carbonates (Wu *et al.*, 2011).



**Figure 2.13.** Likely position of the epoxide to be attacked during cycloaddition reaction.

The attached steric congestion around the epoxides has significant effect on the cycloaddition reaction with  $\text{CO}_2$  to produce organic carbonate. The presence of steric compounds reduces the activity of epoxides. As such, the activity of the terminal epoxide is hindered by the number of alkyl group attached to epoxides. Ethylene oxide (EO) showed higher conversion rate as compared to epoxides with high number of the attached linear alkyl group including PO and butylene oxide (BO). Internal epoxides such as cyclohexene oxide (CHO) has high tendency to convert to polycarbonate as compared to other epoxides such as PO and styrene oxide (SO) with preference to produce cyclic carbonates. Low preference of CHO to produce cyclic carbonate ring may be due to strain imposed by the adjacent cyclohexyl group (Darensbourg and Phelps, 2005; Pescarmona and Taherimehr, 2012). Wei-Li *et al.* (2014) investigated cycloaddition reaction of  $\text{CO}_2$  and various epoxide to synthesise cyclic carbonates and found that the activity of epoxides decreases in the following order  $\text{EO} > \text{ECH} > \text{SO} \approx \text{PO} > \text{CHO}$ . Similarly, Dai *et al.* (2010) found that the reactivity of the substrates investigated in the order of  $\text{ECH} > \text{EO} > \text{SO} \approx \text{PO} > \text{BO} > \text{CHO}$ .

Due to high thermodynamic stability of  $\text{CO}_2$ , the major obstacle in the utilisation of  $\text{CO}_2$  as intermediate feed stock for organic carbonates syntheses is the ability to activate  $\text{CO}_2$  in its low energy level (Sakakura *et al.*, 2007). In addition to the activity of high energy starting materials such epoxide to react with the inert  $\text{CO}_2$  in cycloaddition reaction to produce cyclic carbonates, harsh reaction conditions is often required to facilitate

and initiate the activation of CO<sub>2</sub>. Several reports have shown that cyclic carbonates are thermodynamically favoured as compared to polycarbonates syntheses from the reaction of CO<sub>2</sub> and epoxides (Srivastava *et al.*, 2006; Yasuda *et al.*, 2006). Heterogeneous catalytic process of cyclic carbonates syntheses generally requires harsh reaction conditions as compared to homogeneous catalytic processes. Yasuda *et al.* (2006) reported that from an industrial point of view, a temperature range of 423–473 K is preferable for cycloaddition reaction of epoxides and CO<sub>2</sub> in the presence of heterogeneous catalysts since the reaction is exothermic. Consequently, reaction carried out at elevated temperature favours the selectivity towards the formation of cyclic carbonates. However, reaction of epoxides and CO<sub>2</sub> at low temperature will increase the tendency of polycarbonate formation. Aresta *et al.* (2003) reported that the efficiency of organic carbonates syntheses depends on temperature and solvents. At 100°C, no SO yield was observed, but as the temperature increases, the percentage yield of SC increases. At an optimum temperature of 135°C, 80% yield of SC was obtained. However, low yield (15.7%) of PC was obtained in the absence of CH<sub>2</sub>Cl<sub>2</sub>.

Cyclic carbonate synthesis under the supercritical CO<sub>2</sub> condition rather than CO<sub>2</sub> gas phase can be advantageous for maintaining a good contact with reaction mixture. Therefore, control selectivity, enhanced mass and heat transfer, increased catalyst lifetime and regeneration, facilitate easier separation and process intensification (Baiker, 1999). At a varying reaction temperature, the amount of CO<sub>2</sub> required for the cycloaddition reaction would vary significantly.

Several reports have described the effect of pressure on the cycloaddition reaction for the syntheses of cyclic carbonates. Yasuda *et al.* (2002) carried out a visual observation of PC synthesis under a scCO<sub>2</sub> condition using a sapphire window reactor and found that PO and scCO<sub>2</sub> formed a uniform phase at the initial stage of the reaction while the PC was

separated out from the supercritical phase after the reaction. Subsequently, Song *et al.* (2008); Liang *et al.* (2011); Shi *et al.* (2013) studied the cycloaddition reaction under scCO<sub>2</sub> condition using a view reactor cell. It was observed that two separate phases were present in the reactor vessel under experimental condition. The top phase consists of high concentration of CO<sub>2</sub>, and bottom phase consists of PO and less concentration of CO<sub>2</sub>. An increase in CO<sub>2</sub> pressure favoured the organic carbonate synthesis as the concentration of CO<sub>2</sub> in the bottom phase increased. On the other hand, decrease in the PO concentration in the bottom phase due to an increase in the pressure above the optimum, which retards the interaction of PO and CO<sub>2</sub> that reduced the reaction rate. In addition, an increase in the CO<sub>2</sub> pressure above the required optimum pressure for cycloaddition reaction of epoxide and CO<sub>2</sub> could lead to the dilution of reaction mixture and reduce the efficiency of cyclic carbonate formation. On the other hand, using CO<sub>2</sub> pressure below the optimum level could lead to an increase in the formation of side products (Pescarmona and Taherimehr, 2012).

Subsequently, several reports have shown that reaction time had a remarkable effect on the syntheses of organic carbonates from cycloaddition reaction of PO and CO<sub>2</sub>. In heterogeneous catalytic process, longer reaction time is indispensable as compared with most homogeneous catalytic system. Yamaguchi *et al.* (1999) investigated aluminium and magnesium (Al-Mg) mixed oxide for cyclic carbonate synthesis at reaction time 24 h, a quantitative yield of cyclic carbonate was obtained from the reaction of CO<sub>2</sub> and corresponding epoxide.

### **2.8. Catalytic Activity and Selectivity for Cyclic Carbonates Syntheses**

Catalyst is defined as a substance which increases the rate of reaction without itself undergoing a permanent chemical change. Catalyst can be classified as homogeneous catalysts (metal halides and organic solvents)

and heterogeneous (metal oxides and zeolites). When the catalyst is in the same phase as the reactants and no phase boundary exists, it is called a homogeneous catalyst. Homogeneous catalysis can take place either in the gas phase or liquid phase. On the other hand, the catalyst is termed heterogeneous if the phase boundary separates the catalyst from the reactants. In other words, catalyst is a substance that lowers activation energy to speed up the rate of chemical reaction. The formation of polymeric carbonates requires lower activation energy as compared to the syntheses of cyclic carbonates (Darensbourg, 2007). Therefore, catalysts play a major role in the selectivity of desired organic carbonate. Understanding the catalytic activity is an important factor for designing novel catalyst with an improved catalytic performance for the reaction of epoxides and CO<sub>2</sub> to produce selective organic carbonate.

Development of efficient, highly selective, stable and reusable catalysts for cyclic carbonate synthesis remains a major challenge. Several catalysts including salen complex (Paddock and Nguyen, 2001), Lewis acids and base (Sun *et al.*, 2005), transition metal complex (Lu *et al.*, 2002), metal and mixed oxides (Aresta *et al.*, 2003; Yano *et al.*, 1997; Yasuda *et al.*, 2006), metal salt, ionic liquid (Sun *et al.*, 2005; Zhang *et al.*, 2006a), oxychlorides (Yasuda *et al.*, 2002), porphyrin (Paddock and Nguyen, 2004), and zeolites (Srivastava *et al.*, 2005b) have been developed and investigated. Heterogeneous and homogeneous catalysts, co-catalysts and role of solvents for the cyclic carbonate synthesis are discussed in the following section.

### **2.8.1. Catalytic Activity of Homogeneous Catalysts for Cyclic Carbonates Syntheses**

Several homogeneous catalysts have been reported for the syntheses of cyclic carbonates from reaction of epoxide and CO<sub>2</sub>. Homogeneous catalysts show higher catalytic activity for the syntheses of cyclic carbonates. Examples of homogeneous catalysts that have been

developed for cyclic carbonate synthesis include organic base catalysts, metal halides and salen metal complexes.

### 2.8.1.1. Organic Base and Metal Halide Complexes

Salts and metal halides catalysts such as quaternary ammonium salts, imidazolium salts, bis(triphenylphosphine)immonium (PPN) salts, Schiff base, rhenium complexes and phosphine adducts of zinc halides have been applied for cyclic carbonate synthesis. Calo *et al.* (2002); Sun *et al.* (2004); Fujita *et al.* (2010) investigated quaternary ammonium salts as cheap and effective homogeneous catalysts for cycloaddition reaction of CO<sub>2</sub> and various epoxides using tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBACl) and tetrabutylammonium iodide (TBAI) as catalysts with or without organic solvent such as tert-butylhydroperoxide (TBHP). A quantitative yield (90%) of propylene carbonate was achieved in the presence of TBAB or TBAI at 60°C reaction temperature and 1 bar CO<sub>2</sub> pressure. However, high conversion (99%) of styrene oxide and low yield (33-39%) of styrene carbonate were achieved in presence of TBHP as an oxidant at a reaction condition of 80°C and 10-150 bar for 6 h. It was reported that an increase in CO<sub>2</sub> pressure decrease the rate of reaction for cyclic carbonate formation.

Ra *et al.* (2007) reported the synthesis of styrene carbonate from carboxylation of styrene oxide in the presence of quaternary onium salts including tetraalkylammonium and tetraalkylphosphonium halides in ionic liquids such as 1-*butyl*-3-methylimidazolium tetrafluoroborate (bmimBF<sub>4</sub>). It was reported that tetrabutylphosphonium bromide (Bu<sub>4</sub>PBr) showed high activity in the presence of bmimBF<sub>4</sub> with 99.4% yield of styrene carbonate at 2 h reaction time, 120°C reaction temperature and 140 bar CO<sub>2</sub> pressure. It was highlighted that catalytic activity increases with an increase in CO<sub>2</sub> pressure. Similarly, Peng and Deng (2001) employed *n*-butylpyridinium (BPy) salts as a catalyst in the presence ionic liquid bmimBF<sub>4</sub> without organic solvents for cyclic carbonate synthesis and achieved 100% conversion of propylene oxide, 100% selectivity and



91.8% yield of propylene carbonate at an optimum reaction condition of 110°C, 25 bar for 6 h. However, it was reported that insufficient or excessive amount of CO<sub>2</sub> reduce the efficiency of the rate of reaction. Sun *et al.* (2009) reported the influence of water in homogenous catalytic process for the syntheses of cyclic carbonates, in the presence of *hexyl*-triphenylphosphonium bromide (PPh<sub>3</sub>HeBr) catalyst using water as a solvent. The process recorded high conversion (99.6%) of propylene oxide and high yield (89%) of propylene carbonate. It was observed that the activity of ionic liquid was remarkably improved in the presence of water, leading to high efficiency of cyclic carbonate formation as compared to the cycloaddition reaction carried out without water.

Kawanami *et al.* (2003) developed a rapid and effective method of propylene carbonate synthesis using a supercritical CO<sub>2</sub> in the presence of ionic liquid. The reaction was carried out in the presence of 1-*octyl*-3-methylimidazolium tetrafluoroborate (C<sub>8</sub>mimBF<sub>4</sub>) at a reaction condition of 100°C and 140 bar. Nearly 100% yield and selectivity for propylene carbonate and 77 turnover frequency (TOF) was achieved. It was reported that an increase in the efficiency of cyclic carbonate synthesis was due to the higher CO<sub>2</sub> pressure (140 bar). Bu *et al.* (2007) investigated ruthenium bipyridine complex, (2,2-bipy)RuCl<sub>3</sub>(CH<sub>3</sub>OH) together with ammonium salt cetyltrimethylammonium chloride (CTAC) as an efficient catalyst for propylene carbonate synthesis. At reaction condition of 75°C and 30 bar, 98% yield of propylene carbonate was achieved. It was established that the reaction temperature played an important role in the reaction system to achieve high yield. The catalyst was easily recovered and reused for several times without any appreciable change in its catalyst activity. Furthermore, (2,2-bipy)RuCl<sub>3</sub>(CH<sub>3</sub>OH) and CTAC has the advantage of being stable in air and easy method of preparation that could be beneficial for industrial application.

In addition, Kim *et al.* (2005) studied the phosphine adducts zinc halides,  $\text{ZnX}_2\text{L}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{L} = \text{PMe}_2\text{Ph}, \text{PEt}_3, \text{PBU}_3, \text{PPh}_3$ ) as important catalyst for cyclic carbonate synthesis from  $\text{CO}_2$  and epoxides. It was observed that  $\text{ZnBr}_2/\text{PPh}_3$  showed high catalytic activity for the addition reaction with 78% yield of ethylene carbonate. It was also observed that the yield of ethylene carbonate increased sharply with an increase in temperature, however, a decrease in the ethylene carbonate formation was observed with an increase in molar ratio of reactants. The catalytic activity was not significantly affected by the substitution of phosphine ligands, but was highly depended on the nature of the halide ligands. Sit *et al.* (2005) investigated PPN salts ( $\text{PPN}^+\text{Cl}^-$ , PPN manganese carbonate  $\text{PPN}^+\text{Mn}(\text{CO})_4\text{L}^-$ ,  $\text{L} = \text{CO}, \text{PPh}_3$ ) as an ideal catalyst for cyclic carbonate synthesis from cycloaddition reaction of epoxides and  $\text{CO}_2$ . The reaction was carried out with various epoxides including epihalohydrins, propylene oxide, styrene oxide, isobutylene oxide, butadiene monoxide and 1,2-epoxyhexene.  $[\text{PPN}][\text{Cl}]$ ,  $\text{PPN}^+\text{Mn}(\text{CO})_5^{-6}$  and  $\text{PPN}^+\text{Mn}(\text{CO})_4(\text{PPh}_3)^{-7}$  showed high catalytic activity and selectivity for cyclic carbonate formation. An increase in reactivity of epihalohydrins observed was due to greater electrophilicity of the epoxides carbons that facilitate the ring opening.  $\text{Li}^+\text{Mn}(\text{CO})_4(\text{PPh}_3)^-$  showed much lower catalytic activity under the identical reaction condition which indicated that manganese carbonylate anion  $\text{Mn}(\text{CO})_4(\text{PPh}_3)^-$  alone could not catalyse the coupling reaction of PO and  $\text{CO}_2$ .

Jiang *et al.* (2005) reported rhenium complexes  $\text{Re}(\text{CO})_5\text{X}$  ( $\text{X} = \text{Br}, \text{Cl}$ ) as efficient catalyst for coupling the epoxides and  $\text{CO}_2$  to produce cyclic carbonates in the absence of organic solvent. The catalytic activity of the rhenium complexes including  $\text{Re}(\text{CO})_5\text{Br}$ ,  $\text{Re}(\text{CO})_5\text{Cl}$  and  $\text{Re}_2(\text{CO})_{10}$  were investigated for the syntheses of cyclic carbonates using various epoxides. Up to 96% yield of phenoxypropylene carbonate, 85% yield of phenylpropylene carbonate, and 76% yield of hexylethylene carbonate were achieved from the reaction of corresponding epoxides and  $\text{CO}_2$  in the

presence of  $\text{Re}(\text{CO})_5\text{Br}$  catalyst. It was found that low yield (46%) of propylene carbonate was due to low boiling point ( $34^\circ\text{C}$ ) of propylene oxide. 71% yield of CMEC formation was obtained from coupling reaction of epichlorohydrin with  $\text{CO}_2$  in the presence of  $\text{Re}(\text{CO})_5\text{Br}$  and  $\text{Re}(\text{CO})_5\text{Cl}$  catalysts.  $\text{CO}_2$  pressure played an important role in the syntheses of cyclic carbonates and only 36% yield of CMEC was achieved at low  $\text{CO}_2$  pressure of 10 - 55 bar, whereas, 97% yield was achieved at elevated  $\text{CO}_2$  pressure of 75 bar after 24 h reaction time.

Sun *et al.* (2005) studied the activity of the binary catalyst of zinc bromide ( $\text{ZnBr}_2$ ) and quaternary ammonium iodide ( $n\text{-Bu}_4\text{NI}$ ) for the synthesis of styrene carbonate (SC) from the reaction of styrene oxide (SO) and  $\text{CO}_2$  under supercritical condition. 100% selectivity and nearly 100% yield of SC were obtained at a reaction time of 30 min and reaction temperature of  $80^\circ\text{C}$ . It was highlighted that combined catalysts of  $\text{ZnBr}_2$  and  $n\text{-Bu}_4\text{NI}$  was found to be efficient as compared to the individual  $\text{ZnBr}_2$  or  $n\text{-Bu}_4\text{NI}$  catalysts for the cycloaddition reaction. Similarly, coupling reaction of PO and  $\text{CO}_2$  to produce PC was carried out in the presence of combined catalysts nickel (II) complex  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2\text{PPh}_3/\text{Zn}$  and quaternary ammonium bromide  $n\text{-Bu}_4\text{NBr}$  at reaction condition of  $120^\circ\text{C}$  and 25 bar. 99% yield of propylene carbonate, 100% selectivity and high TOF value of  $3544\text{ h}^{-1}$  was achieved (Li *et al.*, 2003). It was reported that  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2\text{PPh}_3/\text{Zn}/n\text{-Bu}_4\text{NBr}$  catalyst was sensitive to temperature, i.e. at a lower temperature of  $90^\circ\text{C}$ , the yield of propylene carbonate and TOF was decreased, however, the optimum reaction temperature for the PC synthesis was found to be  $120^\circ\text{C}$ .

Several literature have showed that organic base (dimethylamino)pyridine (DMAP) is an efficient and strong Lewis base for the cycloaddition reaction of epoxide and  $\text{CO}_2$  to produce organic carbonates. Paddock and Nguyen (2001); Sankar *et al.* (2004); Shen *et al.* (2004); Shiels and Jones (2007) investigated the activity of organic base DMAP for the synthesis of PC

from addition reaction of PO and CO<sub>2</sub>. Remarkably high conversion of epoxide and yield of PC were achieved. It was observed that the presence of DMAP played an important role in the ring opening of the epoxides for the synthesis of cyclic carbonate. High catalytic activity of DMAP could be attributed to the strong Lewis basic properties that activate both the epoxide and CO<sub>2</sub>. In addition, the combined effects of the Lewis acid metal complex ions with nucleophilic interaction of strong Lewis base DMAP increase the efficiency of cyclic carbonate synthesis. Jing and Nguyen (2007) investigated Lewis acid tin (IV) chloride (SnCl<sub>4</sub>) and Lewis base DMAP as catalyst system for coupling reaction of epoxides and CO<sub>2</sub>. The coupling reaction was carried out under mild reaction condition of 50-75°C reaction temperature, 50 bar CO<sub>2</sub> pressure and 3-5 h reaction time. 100% conversion of PO, 99% yield of PC and high TOF value of 1388 h<sup>-1</sup> were obtained. The high catalytic activity of SnCl<sub>4</sub> and DMAP was attributed to the strong Lewis base. However, it was established that the interaction of organic base and organic solvent such as 2-dichloroethane (DCE) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was unfavourable for cyclic carbonate synthesis and no activity was observed for the cycloaddition reaction.

Kawanami and Ikushima (2000) investigated dimethylformamide (DMF) as a catalyst/solvent for cycloaddition reaction of styrene oxide (SO) and CO<sub>2</sub> to produce styrene carbonate (SC) in the absence of any co-catalyst. It was reported that the rate of reaction for SC synthesis under supercritical CO<sub>2</sub> (scCO<sub>2</sub>) was remarkably higher with 85% yield as compared to the cycloaddition reaction carried out under CO<sub>2</sub> (gas) with 29% yield of SC at the same reaction condition. It was noticed that the solubility of substrate (epoxide) in catalyst/solvent was an important parameter for controlling the reaction system. Aresta *et al.* (2003) performed similar reaction under CO<sub>2</sub> (gas) using DMF as solvent/catalyst. 37% yield of SC was achieved at reaction condition of 135°C temperature, 30 bar CO<sub>2</sub> pressure and 12 h reaction time.

### 2.8.1.2. Salen Metal Complex Catalyst

He *et al.* (2009) studied bifunctional cobalt salen complex containing quaternary phosphonium and Lewis acidic metal centre for the synthesis of cyclic carbonate from reaction of epoxides and CO<sub>2</sub> in the absence of organic solvent. Good yield was achieved at optimum reaction temperature of 100°C and CO<sub>2</sub> pressure of 40 bar. Similarly, Lu *et al.* (2002) investigated the coupling of ethylene oxide and CO<sub>2</sub> to produce ethylene carbonate using (salen)Co and *n*-Bu<sub>4</sub>NBr as catalysts at a reaction temperature of 110°C and 150-160 bar CO<sub>2</sub> pressure with TOF of 1320 h<sup>-1</sup>. Shen *et al.* (2002) described the production of various cyclic carbonates from the reaction of corresponding epoxides and CO<sub>2</sub> using binaphthyldiamino (salen)Co(II) complex catalyst and DMAP as co-catalyst. 80% yield of propylene carbonate was achieved at 100°C reaction temperature and 35 bar CO<sub>2</sub>. Similarly, Paddock and Nguyen (2004) investigated the chiral (salen) cobalt (III) catalyst for the syntheses of cyclic carbonates in the presence of DMAP as a co-catalyst. Remarkably high yield and 100% selectivity of cyclic carbonates were achieved from addition reaction of terminal epoxides and CO<sub>2</sub> at 100°C and 25 bar.

However, despite high catalytic activity of homogeneous system for the syntheses of cyclic carbonates, homogeneous catalysts suffer several limitations include high cost of catalyst production, multi-step process, high cost of separation of product from the reaction mixture, potential production of toxic specie, use of co-solvent, problem of catalyst reusability and instability of the catalyst under room condition (Adeleye *et al.*, 2014; Dai *et al.*, 2010; Sankar *et al.*, 2004). Therefore, the development of solvent free heterogeneous catalytic system is highly desirable in greener process route for valuable chemical synthesis. It offers numerous benefits that eliminate most shortcomings of homogeneous catalytic processes. The solvent free heterogeneous catalytic system is therefore economically viable and safer process that

eliminates the risk to human health and the environment (Anastas *et al.*, 2001). On the other hand, limitations of heterogeneous system include lack of reactor design flexibility and the use of high amount of catalyst.

### **2.8.2. Catalytic Activity of Heterogeneous Catalysts for Cyclic Carbonates Syntheses**

Development of an efficient, cheap, reusable and nontoxic heterogeneous catalyst for cycloaddition reaction of epoxides and CO<sub>2</sub> to produce cyclic carbonates is receiving a growing interest from academia and industry. Heterogeneous catalysts offer several benefits such as easy handling and easy separation from reaction mixture. Several heterogeneous catalysts including unsupported (bulk) catalysts (graphene oxide, metal and mixed metal oxide, and zeolites) and supported catalysts (polymers and immobilised supported) have been developed and investigated for the cyclic carbonate synthesis. The following section explains the common types and preparation methods of heterogeneous catalysts, and provides a review of the heterogeneous catalytic systems for the syntheses of cyclic carbonates.

#### **2.8.2.1. Heterogeneous Supported Catalysts**

In recent years, the catalytic activity of supported catalysts has been investigated for cyclic carbonates syntheses. Supported catalyst is a solid material with high surface area onto which active catalytic specie are attached. Catalyst performance could be enhanced by immobilising a catalytic active specie (mostly homogeneous catalysts) into suitable supports. The supported catalyst can be inert or participate in the catalytic reaction. Several supported catalysts which include polymer, silica and molecular sieve supported catalysts have been reported for the syntheses of cyclic carbonates.

Kim *et al.* (2002) studied polymer supported catalyst such as poly(4-vinylpyridine) (PVP) supported with zinc bromide as an active catalyst for

the synthesis of ethylene carbonates from the cycloaddition reaction of CO<sub>2</sub> and ethylene oxide (EO). The catalyst exhibited 100% selectivity and 53% yield of ethylene carbonate. Similarly, Alvaro *et al.* (2005) examined the performance of polymeric Al(salen) complexes such as polystyrene (Al(salen)PS) and poly-ethylene glycol bismethacrylate (Al(salen)PEA) in the presence of organic base (N-methylimidazole or N,N-dimethylaminopyridine) for the synthesis of styrene carbonate. The polymeric Al(salen)PEA complex gave 89% conversion of styrene oxide (SO) and 78% yield of styrene carbonate at a reaction temperature of 80°C and 100 bar CO<sub>2</sub> pressure.

Barbarini *et al.* (2003) investigated silica-molecular sieve supported catalysts including silica supported guanidine (MCM-41-MTBD) catalyst prepared by covalently bonding of 7-methyl-1,5,7-triazabicyclo[4,4,0]dec-5-ene, (MTBD) and molecular sieve (MCM-41) for the styrene carbonate synthesis. 92% selectivity and 90% yield of styrene carbonate were achieved at 140°C and 50 bar CO<sub>2</sub> pressure. Although, the styrene carbonate yield was lower over MCM-41-MTBD catalyst than when the homogeneous counterpart (MTBD) was used. The MCM-41-MTBD is desirable due to the easy catalyst recovery and reusability. Similarly, Zhang *et al.* (2006b) investigated the use of silica (SiO<sub>2</sub>) supported organic base catalysts (SiO<sub>2</sub>/MTBD) for the synthesis of propylene carbonate and 99% conversion of PO and > 99% selectivity of PC was achieved at 20 bar CO<sub>2</sub> pressure and 150°C reaction temperature. Furthermore, Srivastava *et al.* (2005a) investigated the adenine-modified microporous silica (Ti-SBA-15-pre-Ade) catalyst for cyclic carbonates syntheses. The catalyst showed high activity for the cycloaddition reaction of epoxides and CO<sub>2</sub>, and reported 95% conversion of PO, 100% selectivity and 81% yield of PC at a reaction temperature of 120°C and 69 bar CO<sub>2</sub> pressure.

Xiao *et al.* (2006) studied addition reaction of PO and CO<sub>2</sub> to produce PC over ionic liquid (3-*n*-butyl-1-propyl-imidazolium)-grafted SiO<sub>2</sub> catalyst,



98% selectivity and 95% yield were achieved. Similarly, Wang *et al.* (2006) investigated SiO<sub>2</sub>-supported quaternary ammonium and imidazolium salts as catalyst for cycloaddition reaction and reported 99% selectivity and yield of propylene carbonate in the presence of SiO<sub>2</sub>/imidazolium salt ([C<sub>4</sub>-mim]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>) catalyst.

Immobilisation of active homogeneous catalysts such as non-metals and metal complexes onto supports (metal oxides, polymers, zeolites, and polystyrene) have been studied for the syntheses of cyclic carbonates (Xiao *et al.*, 2006; Dai *et al.*, 2010; Song *et al.*, 2013). The common mobilisation methods include anchoring (*via* adsorption and coordination, encapsulation and covalent tethering) and chemical fixation *via* electrostatic bond methods. In general, method of immobilisation involved imbedding the active complex onto the supports or grafting the prepared active complex onto the support. Example of catalyst prepared *via* anchoring includes the deposition of carbonyl complexes onto the charcoal, alumina or zeolites, and immobilisation of ligand (Dai *et al.*, 2010). Due to the weak interaction between support and catalyst active complex, catalysts prepared *via* anchoring method of immobilisation exhibit weak stability, particularly when the catalysts are used in the reaction which involves high solubility power. As such, the catalyst reusability was not satisfactory and high amount of catalyst is required for the synthesis of organic carbonate (Dai *et al.*, 2010; Dai *et al.*, 2010b).

Encapsulation is the immobilisation process that does not require interaction between the catalyst and the support. The limitation of this process includes the sterical restrain that hinder the catalyst diffusion out of the pores. However, encapsulation method uses unmodified active catalysts (homogeneous catalyst), and no change in ligand or in the coordination sphere of the catalyst are required during encapsulation process. The encapsulation process is performed *via* synthesis of active catalyst inside a support (cage of porous material). This method is well



known as 'ship in the bottle' technique (Dal Santo *et al.*, 2010). In addition, covalent tethering is another immobilisation method that involves organic ligand covalently bound to the support. However, the ligand has to be modified for the immobilisation process. Chemical fixation *via* electrostatic bond method is accomplished *via* immobilisation of cationic and anionic metal complexes by ion exchange or impregnation into the supports such as zeolites. It is a simple and facile method of grafting ionic catalyst into the supports (Song *et al.*, 2013; Xiao *et al.*, 2006).

Another preparation method of heterogeneous catalyst is support modifications which include grafting and co-condensation methods. The grafting method is performed through grafting the functional organic group into an inorganic support. The common support for grafting process is silica. In the case of co-condensation method, the functional organic groups can be incorporated into the solid support during the silica preparation by co-condensation. The shortcoming of these processes is that comparatively small range of functional organic groups or ligands could be incorporated into the support, because high amount of ligands would interfere with the formation process of the support.

Insoluble ion exchange resins and polystyryl supported catalysts containing an ammonium salt or amino group, PEG600( $\text{Bu}_3\text{NBr}$ )<sub>2</sub> investigated by Du *et al.* (2005), 99% yield and 99% selectivity of PC were achieved at 80 bar  $\text{CO}_2$  pressure, reaction temperature of 100°C and reaction time of 24 h. The polymeric catalysts can be easily recovered and reused several times without any significant loss in its catalytic activity. Table 2.3 shows the summary of supported catalysts for cycloaddition reaction of epoxides and  $\text{CO}_2$  to produce cyclic carbonates.

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**Table 2.3.** Catalytic activity of supported catalysts for cyclic carbonates syntheses.

Epoxides	Catalysts	Solvents	Temp (°C)	P <sub>CO<sub>2</sub></sub> (Bar)	Time (h)	Sel. (%)	Yield (%)	TOF (h)	References
EO	Co-salen-MCM-41	<i>n</i> -Bu <sub>4</sub> NBr	110	125	-	100	85.6	-	Lu <i>et al.</i> (2004)
EO	ZnCl <sub>2</sub> -PVP	-	100	35	1	99.8	33.1	201	Kim <i>et al.</i> (2002)
PO	DMAP-SBA-15	CH <sub>2</sub> Cl <sub>2</sub>	120	3.4	4	100	81	50	Shiels and Jones (2007)
PO	TBD-SiO <sub>2</sub>	-	150	20	20	99.8	99.3	-	Zhang <i>et al.</i> (2006b)
PO	Cr-salen-SiO <sub>2</sub>	-	140	34-39	3	-	41	330	Ramin <i>et al.</i> (2006)
PO	<i>n</i> -BuPrimBr-SiO <sub>2</sub>	ZnCl <sub>2</sub>	110	15	1	>98	95	2712	Xiao <i>et al.</i> (2006)
PO	ZnCl <sub>2</sub> -chitosan	BMimBr	110	15	1	99	95	-	Xiao <i>et al.</i> (2006)
PO	<i>n</i> -Bu <sub>4</sub> NBr/SiO <sub>2</sub>	-	150	80	10	98	97	9.5	Wang <i>et al.</i> (2006)
PO	BMImBF <sub>4</sub> /SiO <sub>2</sub>	-	160	80	4	99	96	13.3	Wang <i>et al.</i> (2007)
PO	D201	-	100	80	24	99.8	99.2	0.8	Du <i>et al.</i> (2005)
PO	HI-polyaniline	-	115	50	6	-	99.1	-	He <i>et al.</i> (2007)
SO	Guanidine-MCM-41	CH <sub>3</sub> CN	140	50	70	92	90	-	Barbarini <i>et al.</i> (2003)
SO	Adeine-Pr-AlSBA-15	-	120	6.9	4	97.9	96.3	27	Srivastava <i>et al.</i> (2005b)
SO	Adeine-Pr TiSBA-15	-	120	6.9	4	94.6	88.9	22	Srivastava <i>et al.</i> (2005b)
SO	Cr-salen-SiO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	80	100	6	100	74	431	Alvaro <i>et al.</i> (2004)

### 2.8.2.2. Unsupported (Bulk) Heterogeneous Catalysts

The most employed unsupported heterogeneous catalysts for cyclic carbonates syntheses include zeolites, graphene oxide, metal oxides and mixed metal oxides catalysts. Zeolites are highly porous crystalline material and it belongs to the class of aluminosilicate. Tu and Davis (2001) investigated the zeolite X and other solid catalysts such as cesium and potassium-exchanged zeolite X (Cs/KX), magnesium oxide (MgO), alumina-supported cesium oxide (Cs/Al<sub>2</sub>O<sub>3</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) for the syntheses of cyclic carbonates. It was found that most zeolite X catalysts showed poor activity for the cycloaddition reaction of epoxides and CO<sub>2</sub>. However, the zeolite catalytic activity was improved by incorporation of alkali metal oxide clusters into the pores of zeolites. As such, the combination of Cs/KX-Zeolite and MgO catalyst showed an improved catalytic activity for propylene carbonate synthesis with 54% yield. It was suggested that the yield of organic carbonates was influenced by the base strength, porosity and Lewis acidity of the catalysts. Graphene oxide, metal and mixed metal oxides catalysts, applications of metal oxide are discussed in details in the following section

### 2.9. Graphene Oxide

Graphene is a unique 2D single layer of one atom thick sp<sup>2</sup> carbon in which the atoms have a hexagonal arrangement (Geim and Novoselov, 2007; Rao *et al.*, 2009). Graphene's amazing properties are revealed when layers of graphite are reduced to give a single sheet of carbon atoms which is the thinnest material ever made. It is exceptionally strong, transparent to light, yet impermeable to any gas and electronically fascinating (Dreyer *et al.*, 2010; Williams *et al.*, 2008). However, graphene alone does not possess the properties that are required in a range of technological applications. Therefore, in order to enhance its catalytic properties, it is important to blend graphene at the atomic level with active compound to get best performance. By simply decorating graphene with nanocomposite opens up other possibilities for new and unexpected

phenomena (Liang *et al.*, 2010). However, producing sheets of high quality graphene and graphene based nanomaterials in an economical and environmentally benign way is still challenging. The current methods for homogeneously producing graphene nanomaterial composites involve lengthy and time consuming processes that often lack control of synthetic parameters leading to variation in materials properties from batch to batch. Thus, better synthetic approaches are required. Lan *et al.* (2014) investigated graphene oxide (GO) and reduced graphene oxide (r-GO) as efficient catalysts in the presence of co-catalyst tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ) for the synthesis of PC at reaction condition of 22.5 bar  $\text{CO}_2$  pressure, reaction temperature of  $135^\circ\text{C}$  and reaction time of 1 h, 96% yield and 100% selectivity were achieved in the presence of GO catalysts and  $\text{Bu}_4\text{NBr}$  as co-catalysts. However, GO reusability study showed a significant loss in the catalytic activity after each successful reuse.

### 2.10. Metal Oxide Catalysts

Yamaguchi *et al.* (1999) investigated Mg-Al oxide produced by calcination process of hydrotalcites precursors at  $400^\circ\text{C}$  as highly active acid-base catalysts for the cycloaddition of epoxides and  $\text{CO}_2$  to afford cyclic carbonates. High yield (91%) of SC was achieved in the presence of N,N-dimethylformamide (DMF) as a solvent. Yamaguchi and co-worker suggested that high catalytic activity of Mg-Al oxide was due to interaction of acid sites and strong basic sites. It was showed that high  $\text{CO}_2$  pressure did not influence the yield of SC, however, the selectivity of SC was decreased at high reaction pressure and increased amount of by-products (styrene glycol) were formed. In addition, Yasuda *et al.* (2002) studied the catalyst activities of magnesium oxide ( $\text{MgO}$ ), aluminium oxide ( $\text{Al}_2\text{O}_3$ ), magnesium aluminium (Mg–Al) oxide and lanthanide oxychloride ( $\text{LnOCl}$ ,  $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$ ) for PC synthesis from reaction of PO and  $\text{scCO}_2$  with and without organic solvent DMF. It was reported that  $\text{SmOCl}$  showed 97% selectivity and 57% yield of propylene carbonate in the

absence of organic solvent at a reaction temperature of 200°C and 140 bar CO<sub>2</sub> pressure for 8 h reaction time. The reaction was carried out in the presence of DMF, high selectivity and yield (99%) of PC was achieved. Also, 52%, 55% and 74% yield of PC was achieved in the presence of MgO, Al<sub>2</sub>O<sub>3</sub> and Mg-Al oxide, respectively. It was reported that DMF alone showed moderate catalyst activity for PC synthesis under a scCO<sub>2</sub> condition. The presence of DMF as a solvent and co-catalyst promote catalytic activity of the solid catalysts, such as increased the diffusion and the solubility of PC formed in the reaction mixture and influenced the PC synthesis.

In addition, Yasuda *et al.* (2006) also compared the activity of Cs-P-Si oxide catalyst with other metal oxide such as MgO, Mg-Al oxide and SmOCl for PC synthesis from cycloaddition reaction of PO and CO<sub>2</sub>. Cs-P-Si oxide was found to be highly active compared to other catalysts studied and 94% yield of propylene carbonate was obtained. The limitation of Cs-P-Si oxide as a catalyst for organic carbonate synthesis is that the catalyst is not stable enough to serve as a solid catalyst for PC synthesis. It was reported that components of catalyst eluted into the reaction mixture, hence decrease the catalytic performance. Similarly, Bhanage *et al.* (2001) investigated several metal oxides such as MgO, CaO, ZrO, ZnO, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> as catalysts for the cyclic carbonates syntheses from coupling reaction between CO<sub>2</sub> and epoxides in the presence of N,N-dimethylformamide (DMF). La<sub>2</sub>O<sub>3</sub> gave 54% yield and 74.2% selectivity of PC, whilst MgO achieved 52.4% yield and 92% selectivity of PC at a reaction temperature of 150°C, 80 bar CO<sub>2</sub> pressure for 15 h reaction time. Yano *et al.* (1997) performed similar reaction in the presence of MgO catalyst and DMF for the synthesis of cyclic carbonate and reported moderate yields of PC (72%), SC (60%) and EC (41%) under mild reaction condition.

Aresta *et al.* (2003) employed  $\text{Nb}_2\text{O}_5$  as an active catalyst in the presence of DMF and  $\text{CH}_2\text{Cl}_2$  solvents for the syntheses of cyclic carbonates. Better yield of hexene carbonate (HC, 75%), PC (88%) and octene carbonate (OC, 90%) were achieved at a reaction temperature of  $150^\circ\text{C}$  and 50 bar  $\text{CO}_2$  pressure for 12 h reaction time. Dai *et al.* (2010) studied Zn-M-Al oxide ( $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$  and  $\text{Ba}$ ) catalyst fabricated by calcination of the corresponding hydrotalcite (HTC) precursors for coupling reaction between PO and  $\text{CO}_2$  to produce PC. Zn-Mg-Al oxide with molar ratio of 4:1:1 showed better catalytic performance in the presence of triethylamine (TEA). 88.8% yield and 99.2% selectivity of PC were achieved. It was suggested that the activity of the catalyst was due to strong basicity. Furthermore, Murugan *et al.* (2010) presented calcined Mg-Al oxide as an active catalyst for the PC synthesis in the presence of dimethylformamide (DMF) and dimethylamine (DMA) as solvents. The conversion of PO and yield of PC were 56.5% and 41.3%, respectively in the presence of DMF. However, the conversion of PO and yield of PC were 87.7% and 60%, respectively in the presence of DMA and the catalysts can be reused without any loss in catalyst activity.

Machoa *et al.* (2008) investigated transition metal halides, which include  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{FeCl}_3$ , and group (II) metal halides such as  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaBr}_2$  and  $\text{CaI}_2$  as catalysts for the syntheses of cyclic carbonates in the presence of DMF and *tri*-butylamine (TBA) solvents. DMF/ $\text{CoCl}_2$  gave 99.9% conversion of PO and 94.3% selectivity for PC. The reducing order of reactivity of metal halides was found to be  $\text{CoCl}_2 > \text{NiCl}_2 > \text{CaI}_2 > \text{CuBr}_2$ . Carboxylates, sulphates, carbonates and nitrates of metals catalysts are essentially inactive for the cycloaddition reaction of cyclic carbonate synthesis. The catalytic activities of various metal oxides for cycloaddition reaction of various epoxides and  $\text{CO}_2$  is shown in Table 2.4.

**Table 2.4.** Catalytic activity of metal and mixed metal oxides catalysts for cyclic carbonates syntheses

Epoxides	Catalysts	Solvents	Temp (°C)	P <sub>CO<sub>2</sub></sub> (Bar)	Time (h)	Sel. (%)	Yield (%)	Conv. (%)	References
PO	Al <sub>2</sub> O <sub>3</sub>	DMF	150	80	15	6.6	6.6	100	Bhanage <i>et al.</i> (2001)
PO	CaO	DMF	150	80	15	8.1	0.8	9.9	Bhanage <i>et al.</i> (2001)
PO	CeO <sub>2</sub>	DMF	150	80	15	76.9	17.5	22.7	Bhanage <i>et al.</i> (2001)
PO	Cs-P-Si Oxides	Nil	200	80	8	96.0	94.0	97.9	Yasuda <i>et al.</i> (2006)
PO	DMF	DMF	150	80	15	7.9	7.9	100	Bhanage <i>et al.</i> (2001)
PO	La <sub>2</sub> O <sub>3</sub>	DMF	150	80	15	74.5	54.1		Bhanage <i>et al.</i> (2001)
PO	MgO	DMF	150	80	15	92.0	32.1	34.9	Bhanage <i>et al.</i> (2001)
PO	Nb <sub>2</sub> O <sub>3</sub>	DMF	150	50	12	-	88.0	-	Aresta <i>et al.</i> (2003)
PO	ZnO	DMF	150	80	15	92.6	8.7	9.4	Bhanage <i>et al.</i> (2001)
PO	Zn-Si Oxide	TBAB	120	45	6	100	100	-	Ramin <i>et al.</i> (2006)
PO	SmOCl	Nil	200	140	8	58	-	-	Yasuda <i>et al.</i> (2002)
SO	MgO	DMF	150	80	15	17.2	15.8	92.3	Bhanage <i>et al.</i> (2001)
SO	Nb <sub>2</sub> O <sub>3</sub>	DMF	135	50	12	-	80.0	-	Aresta <i>et al.</i> (2003)

### **2.10.1. Preparation and Applications of Unsupported (Bulk) Heterogeneous Catalysts**

Several preparation routes include conventional and unconventional methods of heterogeneous catalysts have been developed and investigated for the synthesis of value added chemicals. Heterogeneous catalysts such as metal and mixed metal oxide can be prepared through physical and chemical processes. The physical methods of preparation involved the simple combination of different metal oxide *via* mechanical mixing. The chemical routes involve strong interaction and chemically bonded formation of metal oxide linkages. Several chemical preparation routes such as coprecipitation, impregnation, sol-gel, wet precipitation (Reddy and Khan, 2005; Debecker *et al.*, 2012), calcination of catalyst precursors (Tomishige *et al.*, 2004) and continuous hydrothermal flow reactor synthesis (Kellici *et al.*, 2010) of heterogeneous catalysts have been reported. Heterogeneous catalysts such as inorganic solids (metals, metal and mixed metal oxides, salts, sulphides and graphene oxide) and organic materials (organic hydroperoxides, ion exchange resins and enzymes) find applications in several processes including hydrogenation (include Haber-Bosch process of ammonia synthesis, methanol and Fischer-Tropsch synthesis), oxidation, dehydrogenation, organic transformation and fine chemical catalysis (Clark, 2002). The methods of preparation of heterogeneous catalysts have significant effects on physical and chemical characteristics such as surface chemistry (acid-base/redox properties), the homogeneity and textural properties of the catalysts. An appropriate preparative route is fundamental and viable for catalytic activity and selectivity for the desired products. Many conventional preparation routes are energy and chemically intensive, time consuming, multi-step and offer poor control of reaction conditions. Hence, a highly efficient method of catalyst preparation is more desirable.



### **2.10.1.1. Continuous Hydrothermal Flow Synthesis (CHFS) Reactor**

The CHFS reactor offers several advantages over conventional reactor for the synthesis of heterogeneous catalysts. Several reports described CHFS reactor as environment friendly, more efficient and controllable method of solid catalysts synthesis (Kellici *et al.*, 2010). The reactor used a flow of superheated water at 400°C and 24 MPa pressure for the production of nanocomposite catalysts in a short time with desirable physical and chemical characteristics. Advantages of CHFS include high throughput, rapid and controllable method of nano-material synthesis (particle size < 500 nm) (Kellici *et al.*, 2010). However, the major disadvantages of CHFS are to operate at high temperature (400°C) and pressure (24 MPa). Therefore, potential danger should never be ignored, adequate safety precautions are highly important.

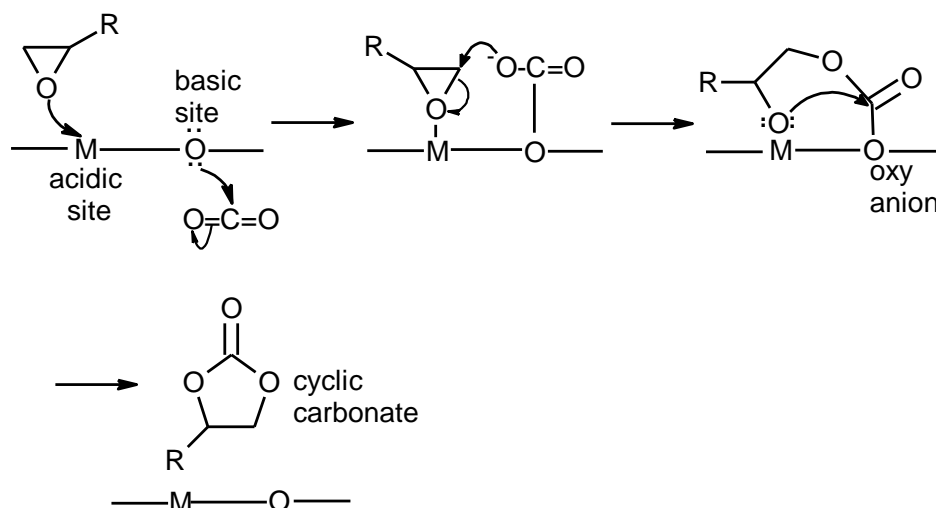
### **2.10.2. Advantages and Disadvantages of Heterogeneous Catalysts**

The requirement of catalyst system for organic carbonates syntheses should not only be limited to enhanced activity and selectivity toward the required organic carbonate products, but should also fulfil the requirement for green and sustainable process. In recent years, heterogeneous catalyst systems have been widely used in chemical industry because of its technical advantages over the homogeneous system. However, both heterogeneous and homogeneous catalysts have advantages and shortcomings. Homogeneous catalyst show high catalytic activity than heterogeneous systems. Nevertheless, the heterogeneous catalysts offers better technical advantages in terms of stability, separation, handling, non-toxic, safe to store and long lifetime. In addition, heterogeneous catalysts could withstand high temperature and pressure, can be disposed safely and reused several times without losing its catalytic activity. In the industrial processes, production cost can be reduced significantly when heterogeneous system of high efficiency is used (Dai *et al.*, 2009). Despite the technical advantages of heterogeneous catalysts, homogeneous catalytic system is highly significant in several industrial applications.

However, the heterogeneous catalytic system has a significant impact on the mechanical design and operation of the processes. Thus, further research should be aimed at design and preparation of heterogeneous catalysts with improved activity and good control of the desired organic carbonate selectivity under a moderate reaction conditions as compared to harsh reaction conditions (high temperature and pressure) generally associated with heterogeneous system.

### **2.10.3. Possible Reaction Mechanism for Syntheses of cyclic carbonates in the Presence of Heterogeneous Catalyst**

The use of heterogeneous catalyst to synthesise cyclic carbonate from the addition reaction of CO<sub>2</sub> and epoxides is currently attracting interest in the last few decades in view of environmental, green chemistry and technical advantages. A number of mechanistic studies have been proposed for the cycloaddition of epoxides and CO<sub>2</sub> in the presence of homogeneous and heterogeneous catalysts (North and Pasquale, 2009; Paddock and Nguyen, 2004; Sankar *et al.*, 2004). In most cases, the studies were demonstrated by means of characterisation with various spectroscopic and analytical instruments. As such, path for the specific reaction mechanism typically depends on the nature of the catalytic system, type of epoxides (substrates) and reaction conditions (Pescarmona and Taherimehr, 2012). The proposed reaction mechanism for the cyclic carbonates syntheses from reaction of epoxides and CO<sub>2</sub> in the presence of heterogeneous metal oxide catalysts is shown in Figure 2.14.



R is an alkyl group. M is a metal (acidic site) atom and O is oxygen (basic site) the atom of metal oxide catalyst

**Figure 2.14.** Possible reaction mechanism for organic carbonates syntheses over heterogeneous catalyst (Yano *et al.*, 1997; Yamaguchi *et al.*, 1999; Yasuda *et al.*, 2002; Dai *et al.*, 2010).

Metal oxide or mixed metal oxide catalysts contain both Lewis acid and Lewis base site for the electrophilic and nucleophilic activation of epoxides and CO<sub>2</sub>. The proposed reaction mechanism using metal oxides and mixed metal oxides catalyst such as Zn-Mg-Al-O (Dai *et al.*, 2010), Mg-Al-O (Yamaguchi *et al.*, 1999), MgO (Yano *et al.*, 1997) and SmOCl (Yasuda *et al.*, 2002) has been investigated for cyclic carbonates syntheses. The metal atom acts as an acid site for the electrophilic activation while oxygen atom acts as a basic site for nucleophilic activation. The addition reaction is initiated by adsorption of CO<sub>2</sub> on the Lewis basic sites to form carbonates specie and the epoxide is independently coordinated on the acid site surface. The carbon atom of epoxide is attacked by a carboxylate anion that leads to the ring opening of epoxide to form oxy-anion specie. Dissociation of metal oxide (catalyst) from the oxy-anion specie leads to a ring closure and desorption of cyclic carbonate as a product. The kinetic study of the addition reaction of epoxides and CO<sub>2</sub> is based on the rate equation postulated by Langmuir-Hinshelwood mechanism, where

epoxides and CO<sub>2</sub> are independently adsorbed on acidic site and basic site, respectively (Yamaguchi *et al.*, 1999).

### **2.11. Catalytic Reactors for Organic Carbonates Syntheses under Supercritical Conditions**

Heterogeneous catalytic processes of organic carbonate synthesis under supercritical conditions required harsh reaction condition such as high pressure and temperature. However, potential danger should never be ignored and adequate safety precautions are highly important. Suitable reactors for organic carbonate synthesis under supercritical condition can be classified into two types according to the mode of operation, batch reactors and continuous flow reactors. Batch reactors for organic carbonate synthesis are closed system which contain a measured quantity of catalyst and the substrate (epoxide), maintained at specific temperature to which a required supercritical fluid (scCO<sub>2</sub>) reactant is introduced at a given instant. The efficiency of the reaction can be determined with the change in the total pressure with time, alternatively, samples are taken at regular time intervals and analysed. It is an important reactor for investigating several organic carbonates syntheses with an inherently good conversion.

On the other hand, continuous reactor is an open system equipped with a fixed column. In a specific operation and reaction, the column is packed with solid catalyst bed and maintained at specific temperature into which the reactants (epoxide and scCO<sub>2</sub>) are continuously introduced and the products extracted. The rate of reaction is determined by taking and analysing the sample from the reaction mixture at regular time intervals. Hence, it is a suitable reactor for kinetic investigation due to high internal recycle ratio, and good mass and heat transfer. However, continuous flow reactor has a limitation of investigating complex reaction system due to low efficiency (conversion) of organic carbonate.

The limitation of batch reactor includes the external mass transfer from the reaction mixture to the surrounding catalyst surface, which is greatly influenced by mixing of reaction mixture. Therefore, an effective mixing is highly required to minimise the effect of external mass transfer resistance in the synthesis of organic carbonates. Hence, batch reactor equipped with internal recycle where the reaction mixture flows through a fixed catalyst bed would minimise the limitation of kinetic studies due to external mass transfer (Baiker, 1999).

### 2.12. Summary

The market demand for organic carbonates has dramatically increased in recent years due to the significance of organic carbonate as intermediates in several industrial applications. Greener and sustainable heterogeneous catalytic reaction of epoxide and CO<sub>2</sub> to produce organic carbonates is receiving a growing attention from chemical industries in terms of technical advantages of heterogeneous system over the homogeneous processes. In this chapter a detailed literature review has been presented on the syntheses of cyclic carbonates from the reaction of epoxides and CO<sub>2</sub>. Inorganic nanocomposite catalysts (metals and mixed metal oxides) were found to be suitable catalysts for the organic carbonates syntheses from environmental and green chemistry point of view. The effect of various parameters e.g. reaction time and temperature, CO<sub>2</sub> pressure, catalyst systems (homogeneous and heterogeneous catalysts), importance of supercritical CO<sub>2</sub> on the efficiency of cyclic carbonates has been discussed.

## ***CHAPTER 3***

# ***CATALYST PREPARATION AND CHARACTERISATION***

### 3. CATALYST PREPARATION AND CHARACTERISATION

#### 3.1. Introduction

Heterogeneous catalysis is an important tool of greener chemical and sustainability processes. An important attribute of heterogeneous catalysts include high activity, good stability, ability to recover and reuse the catalyst, and its selectivity towards a specific direction of the reaction. Heterogeneous catalysts also referred to as solid catalysts are continually relevant and endlessly fascinating in the world of catalytic process industries. About 90% of world chemical manufacturing industry utilises catalyst in one form or another for their production (Thomas and Thomas 1997). However, industries and academic institutions are profoundly aroused to the challenges of heterogeneous catalysis. The processing methods have a strong influence on the physical and chemical properties (particle size, texture, surface area and composition) of the catalysts. Different combinations of properties are required for different chemical catalysis applications. High thermally stable surface area and porosity of the catalyst are the pre-requisites for most catalytic applications.

Several heterogeneous catalysts such as ceria and zirconia graphene oxide ( $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GO}$  labelled as Ce-Zr-GO), ceria, lanthana and zirconia graphene oxide ( $\text{Ce}_x\text{-La}_y\text{-Zr}_{1-(x+y)}\text{O}_2/\text{GO}$  labelled as Ce-La-Zr-GO), ceria, lanthana doped zirconia ( $\text{Ce}_x\text{-La}_y\text{-Zr}_{1-(x+y)}\text{O}_2$  labelled as Ce-La-Zr-O), ceria doped zirconia ( $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  labelled as Ce-Zr-O), lanthana doped zirconia ( $\text{La}_x\text{-Zr}_{1-(x+y)}\text{O}_2$  labelled as La-Zr-O), lanthana ( $\text{La}_2\text{O}_3$  labelled as La-O) and zirconia ( $\text{ZrO}_2$  labelled as Zr-O) were synthesised using a continuous hydrothermal flow synthesis (CHFS) reactor. Graphene oxide (GO) was prepared using improved method by Hummers and Offerman (1958). Characterisation of all the catalysts including commercially available ceria and lanthana doped zirconia (Ce-La-Zr-O), ceria doped zirconia (Ce-Zr-O), lanthana doped zirconia (La-Zr-O), lanthanum oxide (La-O) and zirconium oxide (Zr-O) catalysts were performed using Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy

(TEM), x-ray photoelectron spectroscopy (XPS), x-ray powder diffraction (XRD) and micromeritics analyser.

### 3.2. Preparation of Heterogeneous Catalysts

Several heterogeneous catalysts such as Ce-La-Zr-GO, Ce-Zr-GO, Ce-La-Zr-O, Ce-Zr-O, La-Zr-O and Zr-O were prepared using CHFS reactor, and GO was prepared using improved method by Hummers and Offerman (1958).

#### 3.2.1. Methods and Chemicals

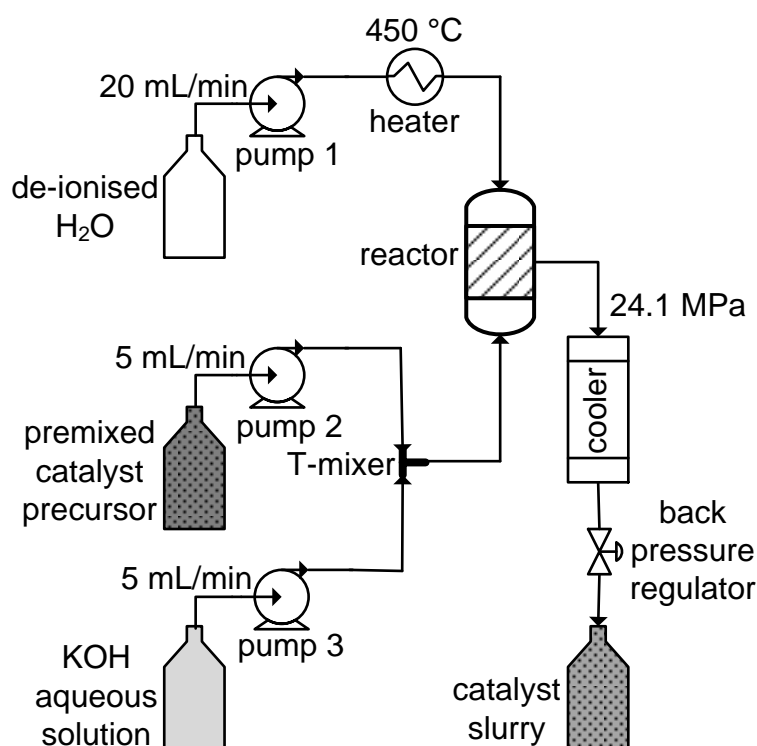
Hydrochloric acid (~37%), sulphuric acid (95+%), graphite powder, sodium nitrate (98+%), cerium (III) nitrate hexahydrate (99.5%), potassium hydroxide (86+%), hydrogen peroxide (>30%) and potassium permanganate (99%) were purchased from Fisher Scientific UK Ltd. Lanthanum (III) nitrate hexahydrate (99.99%) and zirconium (IV) oxynitrate hydrate (99.99%) were procured from Sigma-Aldrich Co. LLC, UK. All chemicals were used without further purification or pre-treatment. The experiments were carried out using deionised water (>10 MΩ).

#### 3.2.2. Continuous Hydrothermal Flow Synthesis (CHFS) Reactor

The basic design of CHFS reactor has been reported previously (Chaudhry *et al.*, 2006; Kellici *et al.*, 2014; Weng *et al.*, 2008). CHFS reactor consists of three high pressure pumps used for the delivery of water and aqueous solution of precursors as shown in Figure 3.1. The tubing and fittings consisted of 1/8 inch 316 SS Swagelok, except the heater, counter-current reactor and the cooler, which were constructed using 1/4 inch fittings. Pump 1 (Gilson 307 fitted with 25 mL pump head) was utilized for delivering deionized water through a custom made 2.5 kW electrically powered pre-heater at a flow rate of 20 mL min<sup>-1</sup>. Pumps 2 and 3 (Varian Pro Star 210 fitted with 5 mL pump head) were used for pumping premixed catalyst precursors and potassium hydroxide (KOH) solution, respectively, at a flow rate of 5 mL min<sup>-1</sup>. In a typical experiment, each



premixed aqueous solution is pumped to meet a flow of KOH (1 M) at a T-junction (Figure 3.1). The mixture then meet superheated water (450°C, 24.1 MPa) inside an in-house built (Kellici *et al.*, 2014) 1/4 inch counter-current reactor (Lester *et al.*, 2006), whereupon the formation of catalyst slurry occurs in a continuous manner. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back pressure regulator.



**Figure 3.1.** Schematic representation of continuous hydrothermal flow synthesis (CHFS) reactor.

### 3.3. Preparation of Metal and Mixed Metal Oxide Catalysts using CHFS Reactor

The metal and mixed metal oxide catalysts prepared using a CHFS reactor include lanthana ( $\text{La}_2\text{O}_3$  labelled as La-O) and zirconia ( $\text{ZrO}_2$  labelled as Zr-O), ceria doped zirconia ( $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  labelled as Ce-Zr-O) and ceria, lanthana doped zirconia ( $\text{Ce}_x\text{-La}_y\text{-Zr}_{1-(x+y)}\text{O}_2$  labelled as Ce-La-Zr-O).

#### 3.3.1. Synthesis of Lanthanum Oxide

Lanthanum (III) nitrate hexahydrate,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and potassium hydroxide (KOH, 1 M) were pumped at a flow rate of  $5 \text{ mL min}^{-1}$  to meet at a T-junction as shown in Figure 3.1. The metal salt mixture then meet superheated water ( $450^\circ\text{C}$ , 24.1 MPa) inside an in-house built counter-current reactor (Kellici *et al.*, 2014), whereupon the formation of  $\text{La}_2\text{O}_3$  occurs in a continuous manner. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back pressure regulator. The solid particles were separated by a centrifuge (5000 rpm) and washed twice with deionized water. The solids were then freeze-dried and labelled as La-O. The La-O catalyst was subjected to heat treatment at temperature of 973 K for 4 h.

#### 3.3.2. Synthesis of Zirconium Oxide

Zirconium (IV) oxynitrate hydrate,  $\text{ZrO}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and potassium hydroxide (KOH, 1 M) were pumped at a flow rate of  $5 \text{ mL min}^{-1}$  to meet at a T-junction as shown in Figure 3.1. The metal salt mixture then meet superheated water ( $450^\circ\text{C}$ , 24.1 MPa) inside an in-house built (Kellici *et al.*, 2014) 1/4 inch counter-current reactor (Lester *et al.*, 2006), whereupon the formation of  $\text{ZrO}_2$  occurs in a continuous manner. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back pressure regulator. The solid particles were separated by a centrifuge (5000 rpm) and washed twice with deionized water. The solids were then freeze-dried and labelled as Zr-O.

The Zr-O catalyst was subjected to heat treatment at a temperature of 973 K for 4 h.

### 3.3.3. Synthesis of Ceria doped Zirconium Oxide Catalyst

Premixed solution of cerium (III) nitrate hexahydrate,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and zirconium (IV) oxynitrate hydrate,  $\text{ZrO}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  at a desired Ce:Zr atomic ratio of 20:80 and potassium hydroxide (KOH, 1 M) were pumped at a flow rate of  $5 \text{ mL min}^{-1}$  to meet at a T-junction as shown in Figure 3.1. The metal salt mixture then meet superheated water ( $450^\circ\text{C}$ , 24.1 MPa) inside an in-house built (Kellici *et al.*, 2014) 1/4 inch counter-current reactor (Lester *et al.*, 2006), whereupon the formation of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  occurs in a continuous manner. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back pressure regulator. The solid particles were separated by a centrifuge (5000 rpm) and washed twice with deionized water. The solids were then freeze-dried and labelled as Ce-Zr-O. The Ce-Zr-O catalyst was subjected to heat treatment at temperature of 973 K for 4 h.

### 3.3.4. Synthesis of Lanthana doped Zirconium Oxide Catalyst

Premixed solution of lanthanum (III) nitrate hexahydrate,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and zirconium (IV) oxynitrate hydrate,  $\text{ZrO}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  at a desired La:Zr atomic ratio of 10:90 and potassium hydroxide (KOH, 1 M) were pumped at a flow rate of  $5 \text{ mL min}^{-1}$  to meet at a T-junction as shown in Figure 3.1. The metal salt mixture then meet superheated water ( $450^\circ\text{C}$ , 24.1 MPa) inside an in-house built (Kellici *et al.*, 2014) 1/4 inch counter-current reactor (Lester *et al.*, 2006), whereupon the formation of  $\text{La}_x\text{-Zr}_{1-(x+y)}\text{O}_2$  occurs in a continuous manner. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back pressure regulator. The solid particles were separated by a centrifuge (5000 rpm) and washed twice with deionized water. The solids were then freeze-dried and labelled as La-Zr-O. The La-Zr-O catalyst was subjected to heat treatment at temperature of 973 K for 4 h.

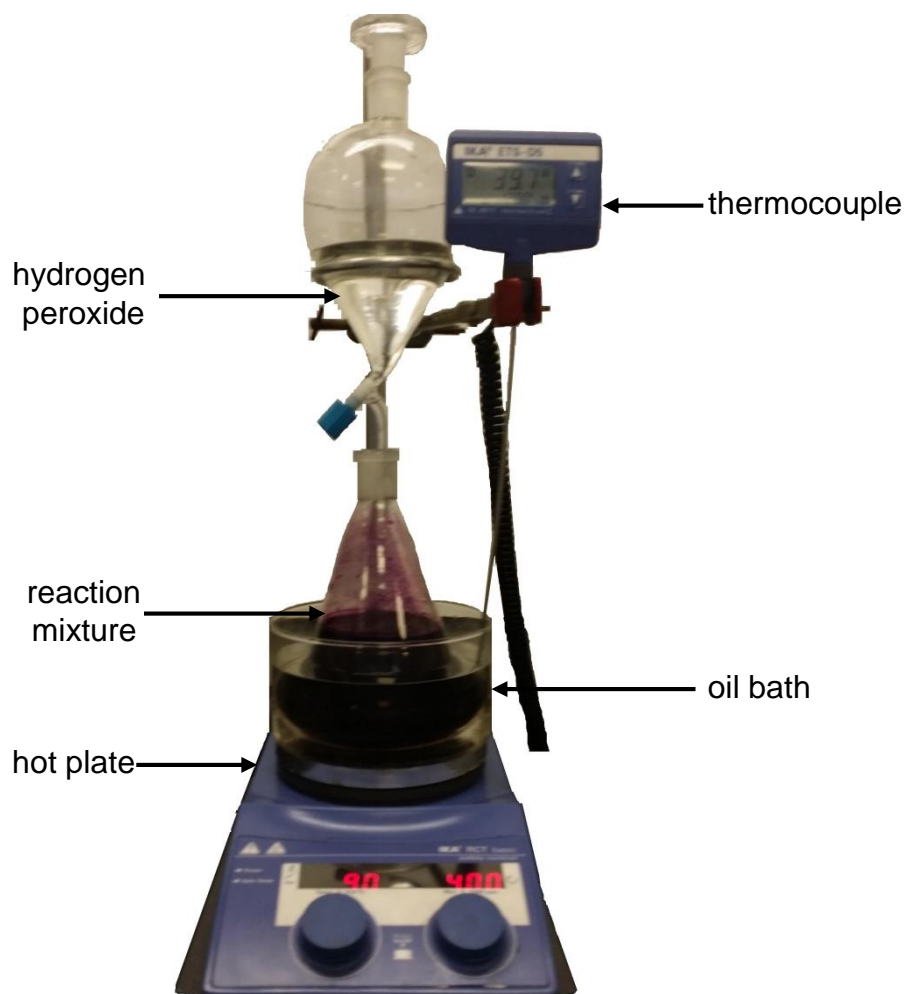
### 3.3.5. Synthesis of Ceria, Lanthana doped Zirconium Oxide Catalyst

Premixed solution of cerium, lanthanum and zirconium salts ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) at a desired Ce:La:Zr atomic ratio of 15:20:80 and potassium hydroxide (KOH, 1 M) were pumped at flow rate of  $5 \text{ mL min}^{-1}$  to meet at a T-junction as shown in Figure 3.1. The metal salt mixture then meet superheated water ( $450^\circ\text{C}$ , 24.1 MPa) inside an in-house built (Kellici *et al.*, 2014) 1/4 inch counter-current reactor (Lester *et al.*, 2006), whereupon the formation of  $\text{Ce}_x\text{-La}_y\text{-Zr}_{1-(x+y)}\text{O}_2$  occurs in a continuous manner. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back pressure regulator. The solid particles were separated by a centrifuge (5000 rpm) and washed twice with deionized water. The solids were then freeze-dried and labelled as Ce-La-Zr-O. The Ce-La-Zr-O catalyst was subjected to heat treatment at a temperature of 973 K for 4 h.

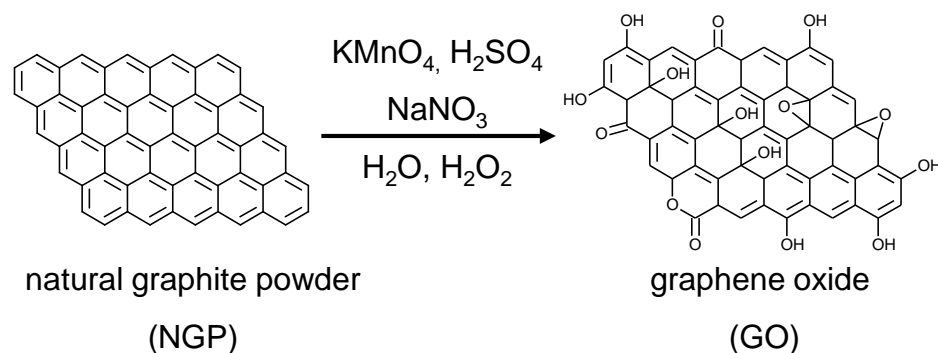
### 3.4. Preparation of Graphene Oxide (GO)

The improved method by Hummers and Offerman (1958) was adopted for the synthesis of graphene oxide from natural graphite powder (NGP) using potassium permanganate as an oxidising agent. The experimental set-up is shown in Figure 3.2. In the typical reaction, 2.5 g of NGP and 2.5 g of sodium nitrate ( $\text{NaNO}_3$ ) were added to 115 mL of sulphuric acid ( $\text{H}_2\text{SO}_4$ ). The black slurry was stirred with a magnetic stirrer for about 15 min in an ice bath. 20 g of potassium permanganate ( $\text{KMnO}_4$ ) was added slowly (for about 5 min) to the reaction mixture. The resulting dark green mixture was left for another 15 min with continuous stirring and the mixture was transferred to an oil bath at  $40^\circ\text{C}$  and stirred at 600 rpm for 90 min. 200 mL of deionised water was added gradually (for about 15 min) to the mixture, followed by addition of 30 mL of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) gradually for about 5 min and 200 mL of deionised water added dropwise for another 15 min. The resulting light brown mixture was stirred at 600 rpm for 15 min at  $90^\circ\text{C}$ . The mixture was cooled to  $15^\circ\text{C}$  and the product (GO) was separated using a centrifuge (5000 rpm, 5 min per cycle). GO

was washed 4 times with dilute hydrochloric acid (HCl) (i.e 10 mL of HCl in 80 mL of deionised water) and 3 times with deionised water to remove any impurities, dried for 24 h using a freeze-drier. The schematic representation of graphite powder transformation to graphene oxide using an improved method by Hummer and Offerman (1958) is shown in Figure 3.3.



**Figure 3.2.** The experimental set-up for preparation of graphene oxide (GO).



**Figure 3.3.** Schematic representation of graphite powder transformation to graphene oxide (GO).

### 3.5. Preparation of Graphene-Inorganic Nanocomposite Catalysts using CHFS Reactor

Graphene-inorganic nanocomposite catalysts including ceria and zirconia graphene oxide ( $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GO}$  labelled as Ce-Zr-GO) and ceria, lanthana and zirconia graphene oxide ( $\text{Ce}_x\text{-La}_y\text{-Zr}_{1-(x+y)}\text{O}_2/\text{GO}$  labelled as Ce-La-Zr-GO) were prepared using a CHFS reactor.

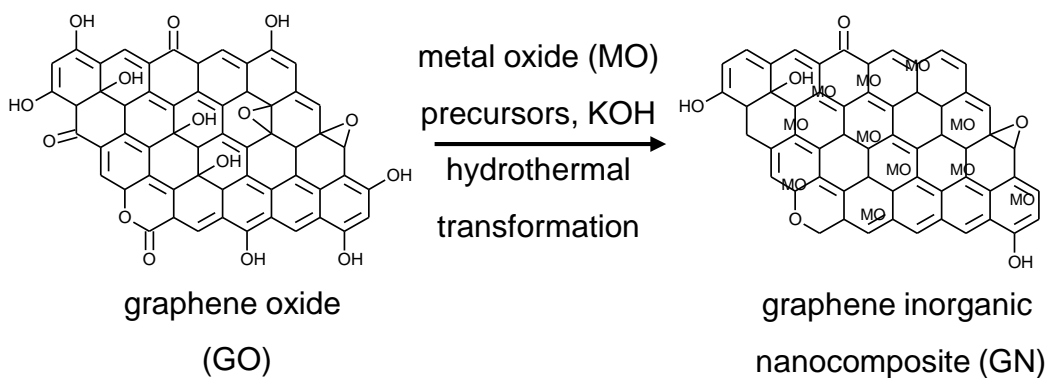
#### 3.5.1. Synthesis of Ceria and Zirconia Graphene Oxide Catalyst

Preparation of ceria doped zirconia graphene oxide (Ce-Zr-GO) was carried out in a CHFS reactor. Pre-sonicated aqueous GO solution, premixed cerium and zirconium salts with Ce:Zr atomic ratios of 20:80 and potassium hydroxide (KOH) base solution were pumped at a flow rate of  $5 \text{ mL min}^{-1}$ . Pre-mixed aqueous solution of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (with a total metal ion concentration of 0.2 M) and a pre-sonicated aqueous solution of GO ( $4 \mu\text{g mL}^{-1}$ ) were pumped to meet a flow of KOH (1 M) at a T-junction (see Figure 3.1). The nominal ratio of metal salt mixture  $\text{Ce}^{3+}/\text{Zr}^{4+}$  to GO was selected to be 1 : 1. This mixture then meet superheated water ( $450^\circ\text{C}$ , 24.1 MPa) inside an in-house built (Kellici *et al.*, 2014) 1/4 inch counter-current reactor (Lester *et al.*, 2006), whereupon the formation of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GO}$  occurs in a continuous manner. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back pressure

regulator. The solid particles were separated by centrifuge (5000 rpm) and washed twice with deionized water. The solids were then freeze-dried and labelled as Ce-Zr-GO. The Ce-Zr-GO catalyst was heat treated at a temperature of 973 K under nitrogen for 4 h. Figure 3.4 shows the schematic representation of Ce-Zr-GO catalyst prepared using a CHFS reactor.

### 3.5.2. Synthesis of Ceria, Lanthana and Zirconia Graphene Oxide Catalyst

Pre-sonicated aqueous GO solution, premixed cerium, lanthanum and zirconium salts with Ce:La:Zr atomic ratios of 15:5:80 and potassium hydroxide (KOH) base solution were pumped at a flow rate of 5 mL min<sup>-1</sup>. Pre-mixed aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (with a total metal ion concentration of 0.2 M) and a pre-sonicated aqueous solution of GO (4 µg mL<sup>-1</sup>) were pumped to meet a flow of KOH (1 M) at a T-junction (see Figure 3.1). The nominal ratio of metal salt mixture Ce<sup>3+</sup>/Zr<sup>4+</sup>/La<sup>3+</sup> to GO was selected to be 1:1. This mixture then meet superheated water (450°C, 24.1 MPa) inside an in-house built (Kellici *et al.*, 2014) 1/4 inch counter-current reactor (Lester *et al.*, 2006), whereupon the formation of Ce-La-Zr-GO occurs in a continuous manner. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back pressure regulator. The solid particles were separated by a centrifuge (5000 rpm) and washed twice with deionized water. The solids were then freeze-dried and labelled as AP (as-prepared Ce-La-Zr-GO). The AP catalysts were subjected to heat-treatment at temperatures of 773, 973 and 1173 K under nitrogen for 4 h and were labelled as HT-500, HT-700 and HT-900, respectively. Figure 3.4 shows the schematic representation of Ce-La-Zr-GO catalyst prepared using a CHFS reactor.



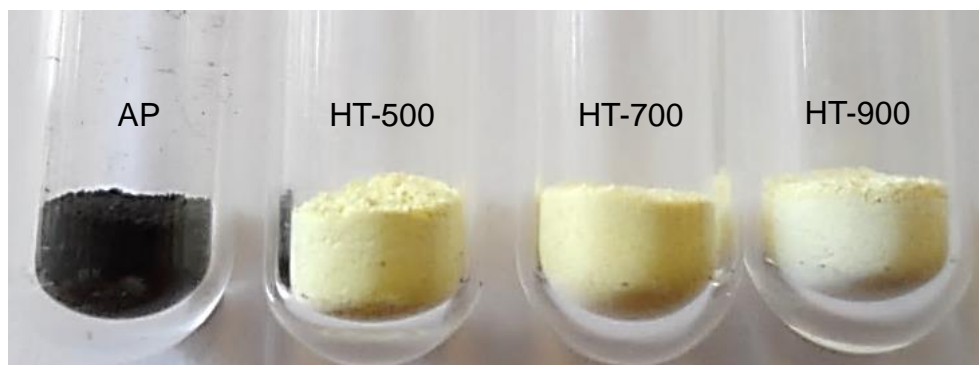
**Figure 3.4.** Schematic representation of graphene inorganic nanocomposite synthesised from graphene oxide and corresponding metal salts in an alkaline medium using superheated water.

### 3.5.3. Catalyst Heat-Treatment

Freeze-drying was performed on all catalysts using a Heto PowerDry PL3000 freeze-dryer. The washed catalysts were frozen in liquid nitrogen and then freeze-dried for 24 h. All the catalysts prepared using a CHFS reactor were heat-treated at different temperatures range from 773–1173 K. Pure metal oxides catalysts including Ce-La-Zr-O, Ce-Zr-O, La-Zr-O and Zr-O were heat-treated at 973 K for 4 h in air using a Carbolite CWF 110 furnace. The graphene nanocomposite samples (Ce-La-Zr-GO and Ce-Zr-GO) and GO were heat-treated for 4 h under nitrogen atmosphere using a Carbolite tube furnace. Ce-Zr-GO and GO catalysts were heat-treated at 973 K, and as prepared Ce-La-Zr-GO (AP) catalyst was heat-treated at temperatures of 773, 973 and 1173 K. The AP catalyst subjected to heat-treatment temperatures of 773, 973 and 1173 K were labelled as HT-500, HT-700 and HT-900, respectively. The photographic image of AP, HT-500, HT-700 and HT-900 catalysts are shown in Figure 3.5. Black powder AP catalyst was heat-treated at 773 and 973 K for 4 h under nitrogen atmosphere and a yellow powder HT-500 and HT-700 catalysts were formed respectively. Further heat-treatment at 1173 K, light yellow catalyst HT-900 was formed. The black colour of AP catalyst is due to the presence of GO. The change of colour from black powder AP



catalyst to yellow HT-500 and HT-700 and light yellow powder HT-900 catalysts may be attributed to the effect of heat-treatment.



**Figure 3.5.** Photographic image of ceria, lanthana and zirconia graphene (Ce-La-Zr-GO) catalysts at different heat-treatment temperatures.

### 3.6. Commercially Available Catalysts

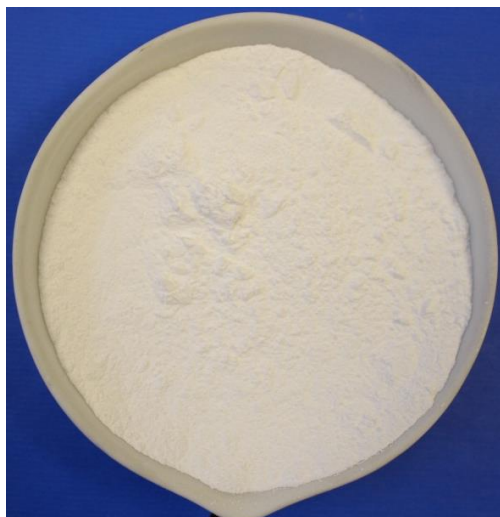
Commercial catalysts such as ceria and lanthana doped zirconia (Ce-La-Zr-O), ceria doped zirconia (Ce-Zr-O), lanthana doped zirconia (La-Zr-O) and zirconium oxide (Zr-O) investigated as part of this research work was supplied by Magnesium Elecktron Limited (MEL) Chemicals, UK. Lanthanum oxide (La-O), magnesium aluminate ( $\text{MgAl}_2\text{O}_4$ , labeled as Mg-Al-O) and Magnesium oxide (MgO) were purchased from Sigma-Aldrich Co. LLC. The photographic images of Ce-La-Zr-O, Ce-Zr-O, La-Zr-O and Zr-O catalysts are shown in Figure 3.6.



ceria, lanthana doped zirconia  
(Ce-La-Zr-O)



ceria doped zirconia (Ce-Zr-O)



lanthana doped zirconia (La-Zr-O)



zirconia (Zr-O)

**Figure 3.6.** Photographic images of commercially available Ce-La-Zr-O, Ce-Zr-O, La-Zr-O and Zr-O catalysts.

### 3.7. Characterisation of Heterogeneous Catalysts

The activity and selectivity of the solid catalysts depend on the structural, textural, particle size characteristics and active sites present on the surface area of the catalyst. Catalyst characterisation provides the basis to investigate the catalytic activity for heterogeneous catalytic processes. The characterisation of heterogeneous catalysts including AP, HT-500,

HT-700 and HT-900 catalysts prepared using a CHFS reactor, commercially available catalysts such as Ce-La-Zr-O, Ce-Zr-O, La-Zr-O and Zr-O catalysts, and GO were performed using Raman spectroscopy (RS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), x-ray powder diffraction (XRD) and micromeritics analyser.

### 3.7.1. Catalysts Characterisation Methods

The catalysts include AP, HT-500, HT-700 and HT-900, Ce-La-Zr-O, Ce-Zr-O, La-Zr-O, La-O, Zr-O and GO. The adopted methods include using analytical instruments such as RS, SEM, TEM, XRD, XPS and micromeritics analyser.

### 3.7.2. Physicochemical properties of commercial catalysts

The commercial catalysts including Ce-La-Zr-O, Ce-Zr-O, La-Zr-O, La-O and Zr-O (except La-O that was purchased from Sigma-Aldrich Co. LLC) used in this research work were prepared by proprietary processes developed by MEL Chemicals Ltd., UK that have been optimised to produce specific particle size distributions and different textural properties (surface area and pore volume). Presented in the Table 3.1 are the physicochemical properties of commercially available catalysts. Zr-O catalyst showed a largest surface area of  $310 \text{ m}^2 \text{ g}^{-1}$ . Ce-La-Zr-O, Ce-Zr-O and La-Zr-O catalysts showed surface area of  $55 \text{ m}^2 \text{ g}^{-1}$ ,  $70 \text{ m}^2 \text{ g}^{-1}$  and  $75 \text{ m}^2 \text{ g}^{-1}$ , respectively, whilst La-O catalyst showed the least surface area of  $22 \text{ m}^2 \text{ g}^{-1}$ . It can be seen from Table 3.1 that La-O catalyst has the smallest total pore volume of  $0.015 \text{ cm}^3 \text{ g}^{-1}$ . Zr-O and Ce-La-Zr-O catalysts exhibited pore volume of  $0.45 \text{ cm}^3 \text{ g}^{-1}$  and  $0.29 \text{ cm}^3 \text{ g}^{-1}$ , whilst Ce-Zr-O and La-Zr-O catalysts showed similar total pore volume of  $0.2 \text{ cm}^3 \text{ g}^{-1}$  and  $0.22 \text{ cm}^3 \text{ g}^{-1}$ , respectively.

**Table 3.1.** Physical and chemical properties of ceria and lanthana doped zirconia (Ce-La-Zr-O), ceria doped zirconia (Ce-Zr-O), lanthanum oxide (La-O), lanthana doped zirconia (La-Zr-O), and zirconium oxide (Zr-O) catalysts.

Properties (units)	Ce-La-Zr-O	Ce-Zr-O	La-O	La-Zr-O	Zr-O
Physical form	Pale yellow powder	Pale yellow powder	White powder	White powder	White powder
Composition (%) <sup>a</sup>	CeO <sub>2</sub> : 17±2 La <sub>2</sub> O <sub>3</sub> : 5±1 ZrO <sub>2</sub> : 78±3	CeO <sub>2</sub> : 18±2 ZrO <sub>2</sub> : 82±2	La <sub>2</sub> O <sub>3</sub> : 100	La <sub>2</sub> O <sub>3</sub> : 10±1 ZrO <sub>2</sub> : 90±1	ZrO <sub>2</sub> : 95±5
Particle size (µm) <sup>a</sup>	1.7	30	0.1	5	5
Surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	55	70	22	75	310
Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	0.29	0.2	0.015	0.22	0.45
Pore diameter (nm) <sup>a</sup>	21.1	11.4	2.7	11.7	5.8
Operating Temperature (K) <sup>a</sup>	673	673	2578	673	673
True density (g cm <sup>-3</sup> )	4.41	4.53	2.14	4.43	3.04
Bulk density (g cm <sup>-3</sup> )	0.51	0.94	0.22	0.82	0.41

<sup>a</sup>Manufacturer data

### 3.7.3. True Density Determination

True density of the solid catalysts was measured using a density bottle. The density bottle was filled with methanol up to the density bottle mark and weighed. A known quantity of the catalyst sample was added to the density bottle and reweighed. The volume of methanol displaced by the catalyst was calculated as the true density of the catalyst. 1 g of catalyst sample was used and density measurements were made in duplicate and average value was reported. The measured true densities of commercially available catalysts including Ce-La-Zr-O, Ce-Zr-O, La-Zr-O, La-O and Zr-O are shown in the Table 3.1.

### 3.7.4. Micrometrics Analysis

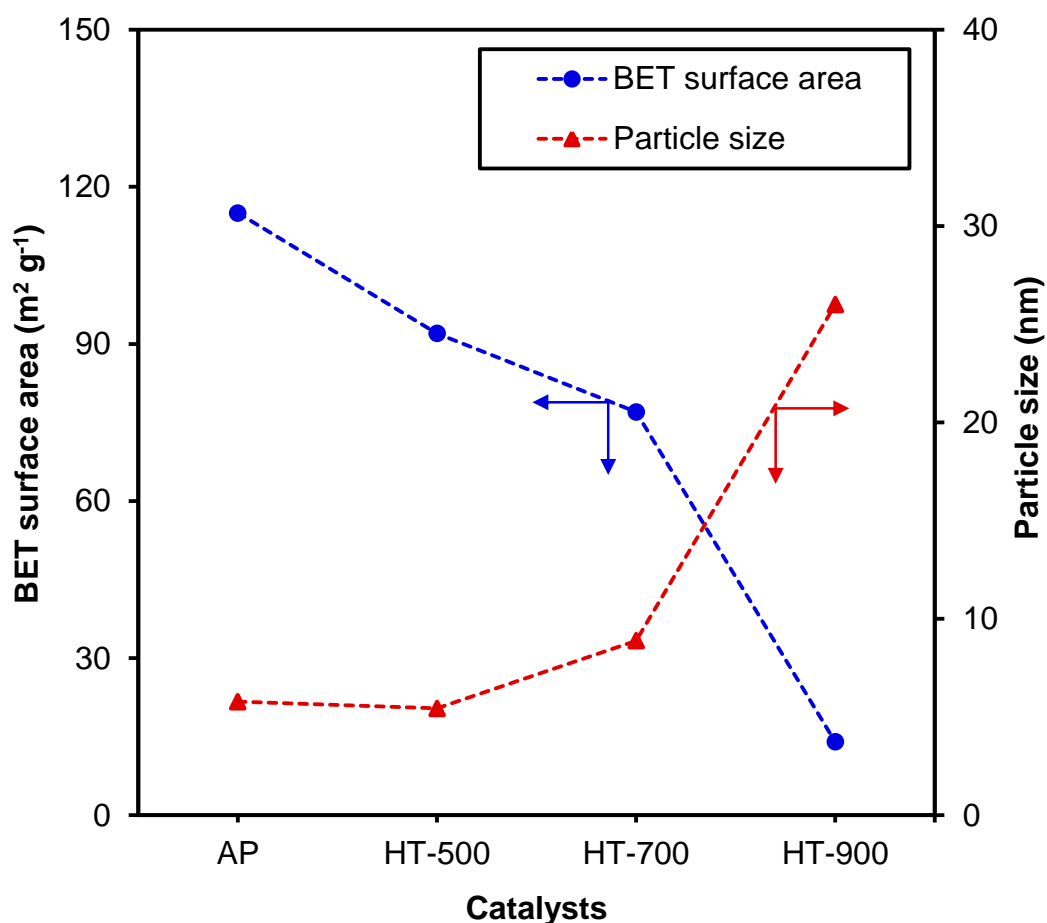
Brunauer-Emmett-Teller (BET) surface area measurements and Barrett–Joyner–Halenda (BJH) adsorption average pore diameter (4V/A) of GO, AP, HT-500, HT-700 and HT-900 were measured by nitrogen adsorption and desorption method using a Micromeritics Gemini VII (surface area and porosity) analyser. Each catalyst was degassed at 373.15 K for 5 h prior to analysis using a Micromeritics FlowPrep 060 sample degas system. The average pore diameter and pore volume were obtained using the Barrett–Joyner–Halenda (BJH) method.

Presented in the Table 3.2 are the BET specific surface area (SSA) of as-prepared (AP) and corresponding heat-treated catalysts (HT-500, HT-700 and HT-900) synthesized *via* CHFS. The observed trends in SSA and particle size are reported in Figure 3.7. GO has largest Brunauer-Emmett-Teller (BET) surface area of  $124 \text{ m}^2\text{g}^{-1}$  and total pore volume of  $0.049 \text{ cm}^3 \text{ g}^{-1}$ . It is noted that sample AP shows the high SSA of  $115 \text{ m}^2 \text{ g}^{-1}$  which decreased to SSA of  $92 \text{ m}^2 \text{ g}^{-1}$  as the catalyst was heat-treated at 773 K (HT-500). Further heat-treatment of the catalyst at 973 K (HT-700) showed a further reduction in the BET surface area ( $77 \text{ m}^2\text{g}^{-1}$ ), and this may be attributed to an increase in the particle size ( $8.88 \pm 1.72$ ) as confirmed from TEM data (Table 3.1). All the catalysts are in mesoporous range

(2–50 nm). The pore volume of AP, HT-500 and HT-700 catalysts are 0.047, 0.036 and 0.038 cm<sup>3</sup> g<sup>-1</sup> respectively, with HT-900 catalyst heat-treated at 1173 K showed lower BET surface area of 14 m<sup>2</sup> g<sup>-1</sup> and total pore volume of 0.007 cm<sup>3</sup> g<sup>-1</sup>.

**Table 3.2.** Physical and chemical properties of graphene oxide (GO), as prepared ceria, lanthana and zirconia graphene oxide (Ce-La-Zr-GO denoted as AP) and AP at different heat-treatment temperatures (HT-500, HT-700 and HT-900).

Properties (units)	GO	AP	HT-500	HT-700	HT-900
Physical form	Black powder	Black powder	Yellow powder	Yellow powder	Yellow powder
Atomic %	O: 24.64	Ce: 2.98;	Ce: 2.4;	Ce: 3.08;	Ce: 2.27;
Composition (XPS)	C: 75.36	La: 1.19; O: 34.99 C: 47.29; K: 0.8; Zr: 12.75	La: 0.99; O: 38.53 C: 41.8; K: 1.29; Zr: 15	La: 1.29; O: 38.72 C: 40.83 K: 0.85; Zr: 15.22	La: 1.02; O: 33.85 C: 49.06; K: 0.13; Zr: 13.68
Mean particle size (nm)	-	5.78 ±1.56	5.44 ±1.39	8.88 ±1.72	26.0 ±8.5
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	124	115	92	77	14
Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.049	0.047	0.036	0.038	0.007
Average pore diameter (nm)	2.37	2.16	2.05	2.19	2.09



**Figure 3.7.** BET surface area and particle size trends of AP and the corresponding heat-treated Ce-La-Zr-GO nanocomposite catalysts.

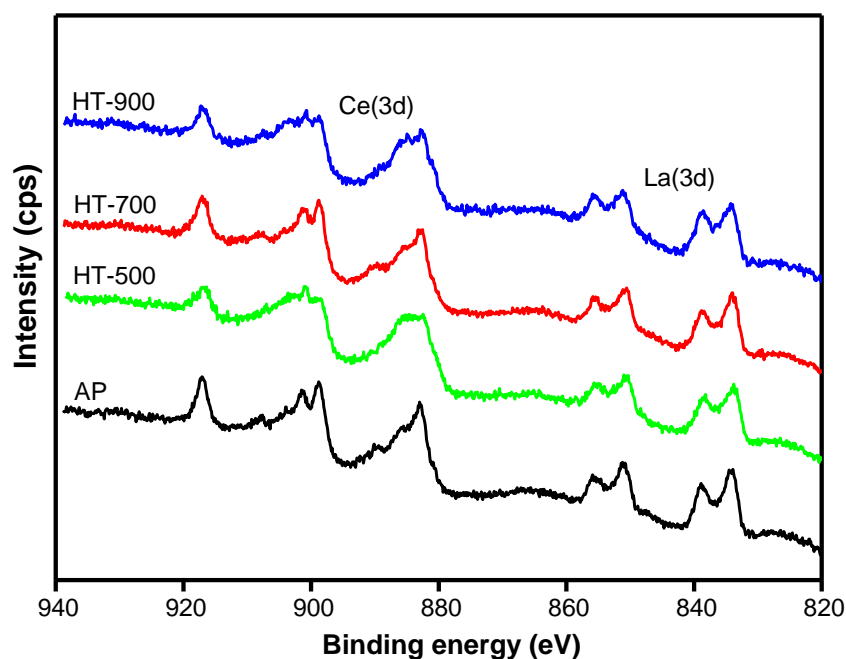
### 3.7.5. X-ray Photoelectron Spectrometry (XPS) Analysis

XPS measurement of GO, AP, HT-500, HT-700 and HT-900 catalysts were performed on Kratos Axis ultra DLD photoelectron spectrometer utilising monochromatic Alka source operating at 144 W. Samples were mounted using conductive carbon tape. Survey and narrow scans were performed at constant pass energies of 160 and 40 eV, respectively. The base pressure of the system is ca.  $1 \times 10^{-9}$  Torr, rising to ca.  $4 \times 10^{-9}$  Torr under analysis of these samples.

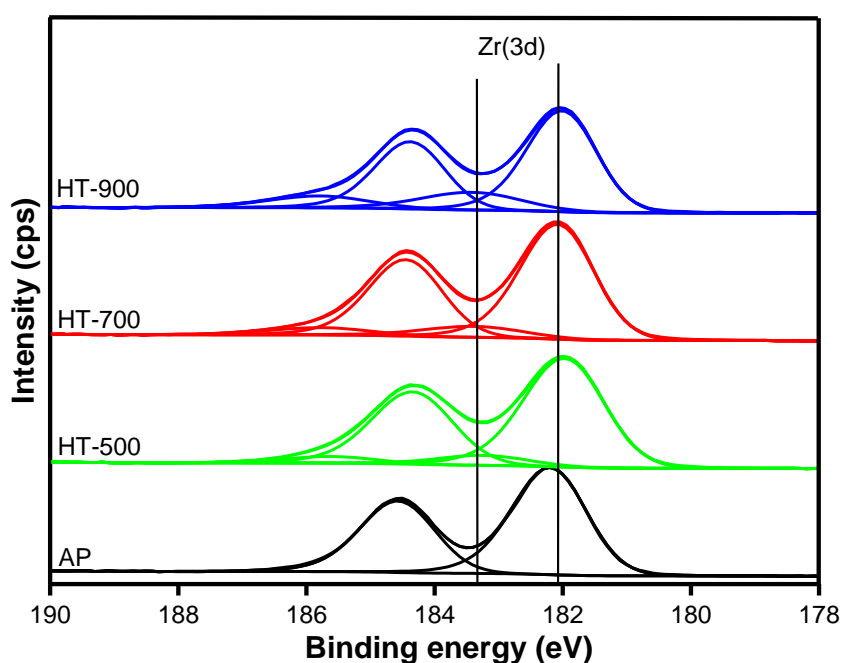
XPS analysis was employed to investigate the changes in the concentration of cerium and zirconium in the lattice, their oxidation states

and the chemical states of graphene oxide (GO) for as-prepared (AP) catalyst and corresponding HT-500, HT-700 and HT-900 heat-treated catalysts. XPS percentage (%) atomic composition showed that GO is predominantly consist of oxygen and carbon atoms (C:O/3:1) and Ce-La-Zr-GO catalysts consist of metals (Ce - cerium, La – lanthanum and Zr – zirconium), K – potassium, C - carbon and O – oxygen atoms as shown in Table 3.2. XPS analysis revealed that the metal ratios for all samples are all very similar. Figure 3.8–3.11 show the XPS spectra of the catalysts. The spin-orbit splitting of the La3d<sub>5/2</sub> peak (ca 4.5 eV) suggests La<sub>2</sub>O<sub>3</sub> is the dominant phase with the binding energy of 856 and 837 eV. In addition, it is noted that cerium (Ce) is present as mixed Ce(III) and Ce(IV) and higher concentration of Ce(IV) are observed in samples labelled as AP and HT500 with respect to other samples at binding energy of 920, 900 and 890 eV as shown in Figure 3.8. Zirconium, on heat-treatment forms two states. State at 182.2 eV is due to ZrO<sub>2</sub>, state at 183.4 eV is due to Zr-OH bonds. The presence of sub oxides is eliminated as these appear at lower binding energies (179-181 eV) as shown in Figure 3.9. Assignment due to Zr-OH is also supported by large O(1s) component at 531.4 eV (Li *et al.*, 1995) in Figure 3.10. C(1s) of GO is severely changed by the decorative effect of Ce-La-Zr-O mixed metal oxide as shown in Figure 3.11.

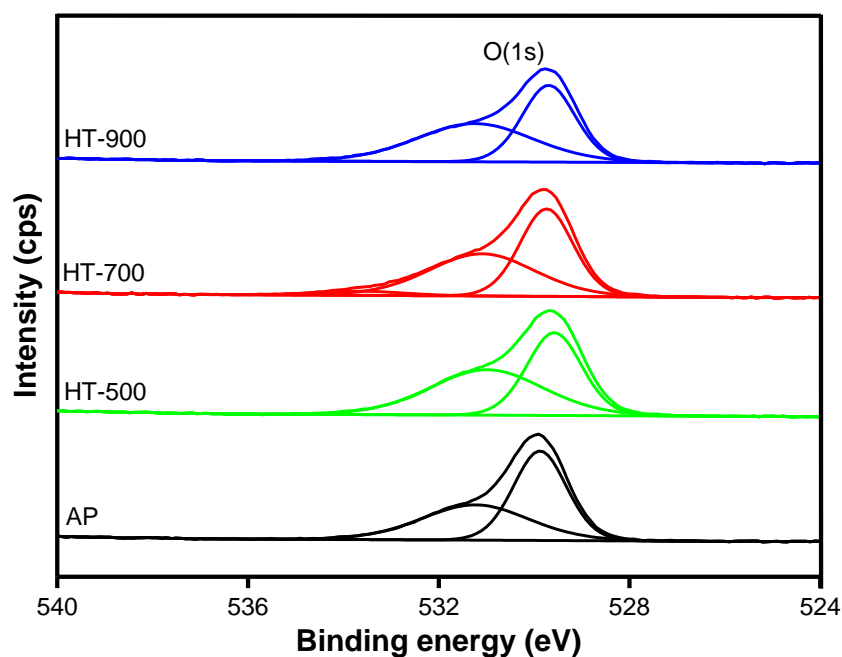




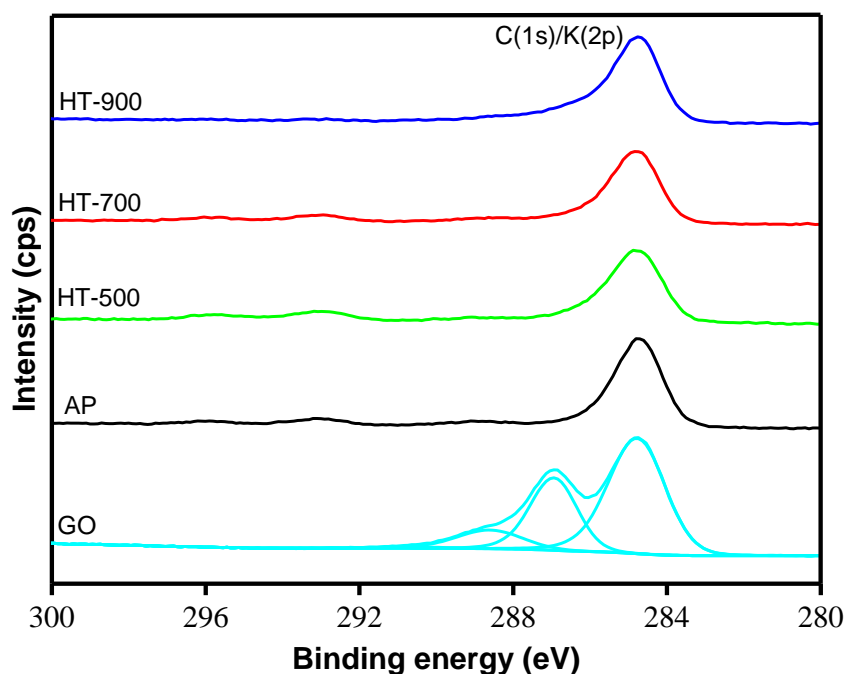
**Figure 3.8.** X-ray photoelectron spectroscopy (XPS) spectra showing devonvoluted Ce(3d) and La(3d) region for the AP, HT-500, HT-700 and HT-900 catalysts.



**Figure 3.9.** X-ray photoelectron spectroscopy (XPS) spectra showing devonvoluted Zr(3d) region for the AP, HT-500, HT-700 and HT-900 catalysts.



**Figure 3.10.** X-ray photoelectron spectroscopy (XPS) spectra showing devonvoluted O(1s) region for the AP, HT-500, HT-700 and HT-900 catalysts.



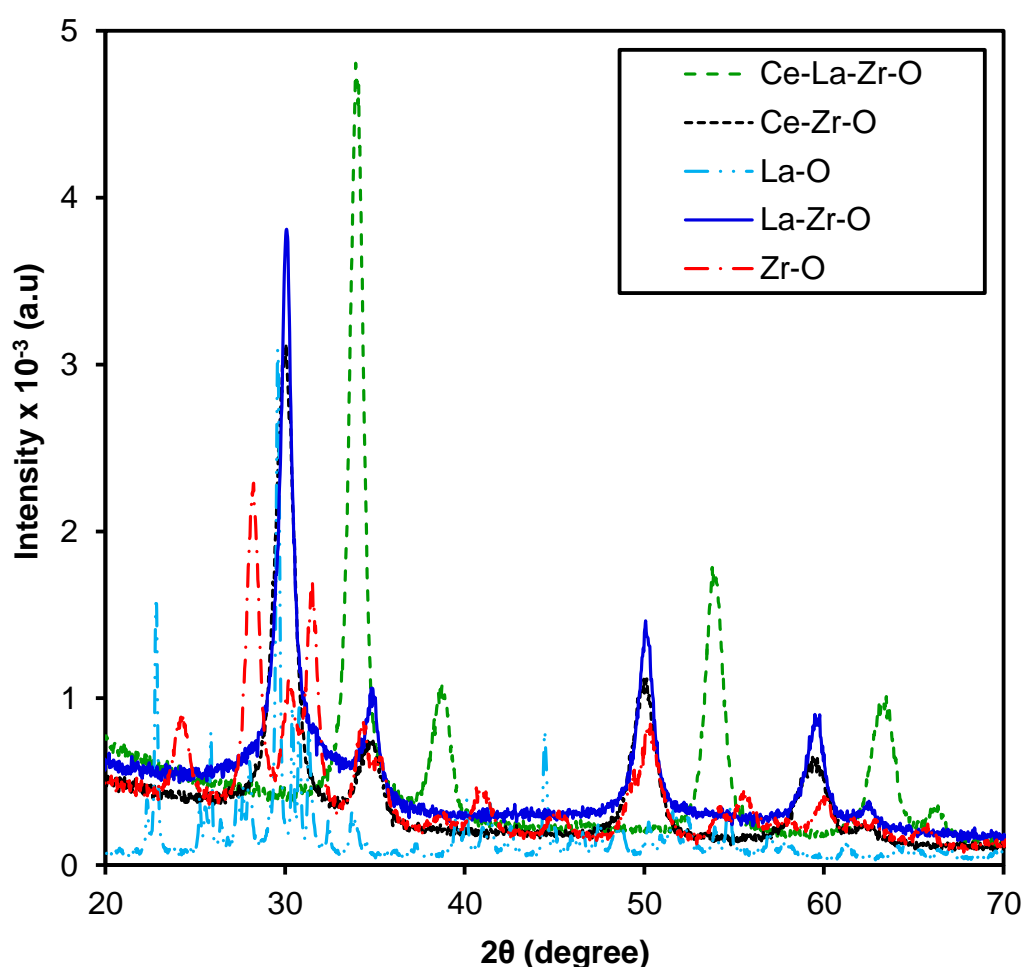
**Figure 3.11.** X-ray photoelectron spectroscopy (XPS) spectra showing devonvoluted C(1s) region for the AP, HT-500, HT-700, HT-900 catalysts and GO.

### 3.7.6. X-ray Diffraction (XRD) Analysis

XRD patterns of commercially available catalysts including Ce-La-Zr-O, Ce-Zr-O, La-Zr-O, La-O and Zr-O were investigated on a Siemens D5000 X-Ray Powder diffractometer analyser operated in  $\theta/2\theta$  geometry. XRD data of as prepared, AP and the corresponding heat-treated catalysts, HT-500, HT-700 and HT-900 synthesised *via* CHFS reactor and GO were collected on a Stoe StadiP transmission diffractometer using Mo radiation (0.7093 angstrom wavelength) set at 50 kV 30 mA using a Germanium 111 monochromating crystal to select K alpha 1. Samples were prepared by sandwiching a small amount of the material between two polymer sheets, clamping into a 3 mm aperture holder and rotating in the X-ray beam. The detector was a Dectris Mythen 1K silicon strip PSD (Position Sensitive Detector). Data were collected by scanning from 2–45  $2\theta$  degree ( $^{\circ}$ ) at 0.5 $^{\circ}$  steps and 30 seconds per step, the step resolution of the data being 0.015 $^{\circ}$ . Diffractometer alignment was checked with LaB<sub>6</sub> standard.

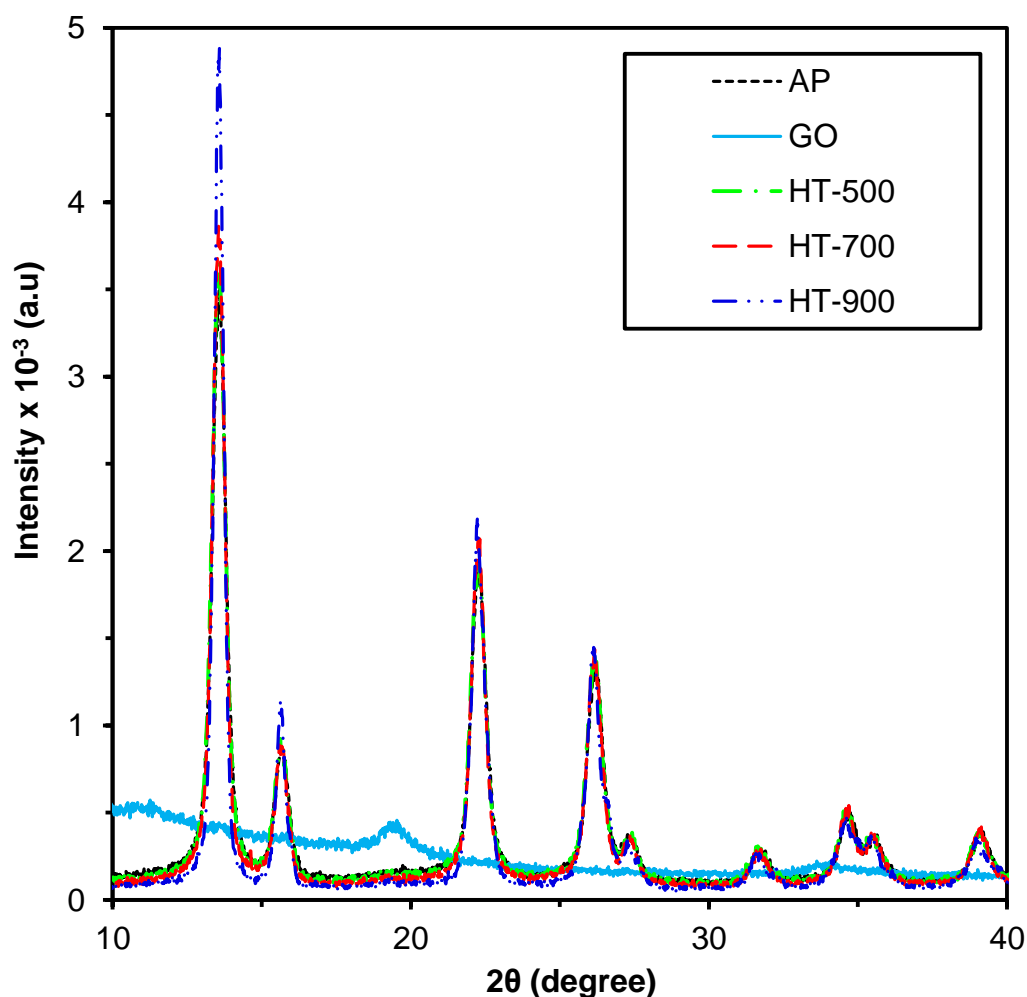
The XRD patterns of commercially available catalysts Ce-La-Zr-O, Ce-Zr-O, La-O, La-Zr-O and Zr-O are presented in Figure 3.12. It is evident from Figure 3.12 that the dopants (ceria and lanthana) have stronger interaction with zirconia. The La-O and Zr-O peaks show low intensity at  $2\theta = 23^{\circ}$ ,  $28^{\circ}$ ,  $30^{\circ}$ ,  $31^{\circ}$ ,  $40^{\circ}$ ,  $44^{\circ}$ ,  $50^{\circ}$ ,  $60^{\circ}$  and  $66^{\circ}$  as compared to Ce-La-Zr-O catalyst that showed higher intensity peaks at  $2\theta = 32^{\circ}$ ,  $34^{\circ}$ ,  $39^{\circ}$ ,  $54^{\circ}$  and  $63^{\circ}$ . Ce-Zr-O and La-Zr-O catalysts have high intensity peaks appeared at  $2\theta = 29^{\circ}$ ,  $32^{\circ}$ ,  $34^{\circ}$ ,  $50^{\circ}$  and  $60^{\circ}$ . These results are in agreement with that reported in the literature (Hu *et al.*, 2007). Surface area and structural characteristics of Zr-O (cubic, monoclinic and tetragonal zirconia) depend on the calcination process. Calcination process at 773 K is identical to amorphous monoclinic zirconia and at 873 K connotes the tetragonal zirconia (Zhao *et al.*, 2002). The processing methods including calcination temperature and incorporation of dopants have a strong influence on the physicochemical properties of the catalysts. As a result, the peaks at  $2\theta = 23^{\circ}$ ,  $28^{\circ}$  and  $31^{\circ}$ , exhibit monoclinic zirconia and the peaks appear at

$2\theta = 30^\circ, 32^\circ, 50^\circ$  and  $60^\circ$  represent tetragonal zirconia. Tetragonal zirconia showed higher thermal stability as compared to monoclinic zirconia. The influence of the dopants thus increases the stability of the catalyst as illustrated in Figure 3.12. The strong peak intensity of Ce-La-Zr-O catalyst could be due to a decrease in crystallinity of the zirconia catalyst and hence the presence of dopants increases the stability of the catalysts. Therefore, Ce-La-Zr-O catalyst exhibited higher stability as compared to the Ce-Zr-O and La-Zr-O catalysts.



**Figure 3.12.** X-ray diffraction (XRD) patterns of ceria and lanthana doped zirconia (Ce-La-Zr-O), ceria doped zirconia (Ce-Zr-O), lanthanum oxide (La-O), lanthana doped zirconia (La-Zr-O) and zirconium oxide (Zr-O) catalysts.

The crystallinity and composition of GO, AP, HT-500, HT-700 and HT-900 nanocomposite catalysts were studied by X-ray powder diffraction (XRD) as shown in Figure 3.13. The XRD patterns for each of the catalysts data sets matched well with  $\text{Zr}_{0.84}\text{Ce}_{0.16}\text{O}_2$  (ICDD standard card no. 38-1437) where the cell and space group given were used as the start model for Le Bail fitting with Rietica (obtained unit cell parameters from La Bail fits are reported in the Appendix A). However, sample HT-900 gave unassigned small peaks from an unidentified phase or phases present. These areas were excluded from Le Bail fitting.



**Figure 3.13.** X-ray diffraction (XRD) spectra of graphene oxide (GO), as prepared (AP) catalyst and the corresponding heat-treated catalysts HT-500 (heat-treated at 773 K), HT-700 (heat-treated at 973 K) and HT-900 (heat-treated at 1173 K).

### 3.7.7. Raman Spectroscopy (RS)

Raman spectra of commercially available catalysts including Ce-La-Zr-O, Ce-Zr-O, La-Zr-O, La-O and Zr-O were recorded using a Renishaw Ramascope 1000 (model: 52699) analyser connected to an optical microscope and a modu-laser source. Raman spectra of catalysts are presented in Figure 3.14. The parameters that affect the Raman bands include crystal size, structure and stresses of a catalyst (Barberis *et al.*, 1997). High intensity and broad peaks appeared at a wavelength ( $\lambda$ ) of  $620\text{ cm}^{-1}$  and  $1060\text{ cm}^{-1}$ , signifies the presence of Zr-O and La-O as the dominant phases of the catalysts. Ce-Zr-O catalyst showed higher intensity and broader peaks at a wavelength ( $\lambda$ ) of  $620\text{ cm}^{-1}$  as compared to Ce-La-Zr-O and La-Zr-O and Zr-O catalysts. However, La-O catalyst showed no peak at  $\lambda = 620\text{ cm}^{-1}$  and higher intensity peak of La-O was observed at  $\lambda = 1060\text{ cm}^{-1}$ . The broad peaks at  $\lambda = 620\text{ cm}^{-1}$  was in accordance with Zr-O catalyst reported in the literature (Liu *et al.*, 2010). The stronger intense peaks may be due to an increase in the surface area of Zr-O catalyst which could have been influenced by the incorporation of dopant into the Zr-O.

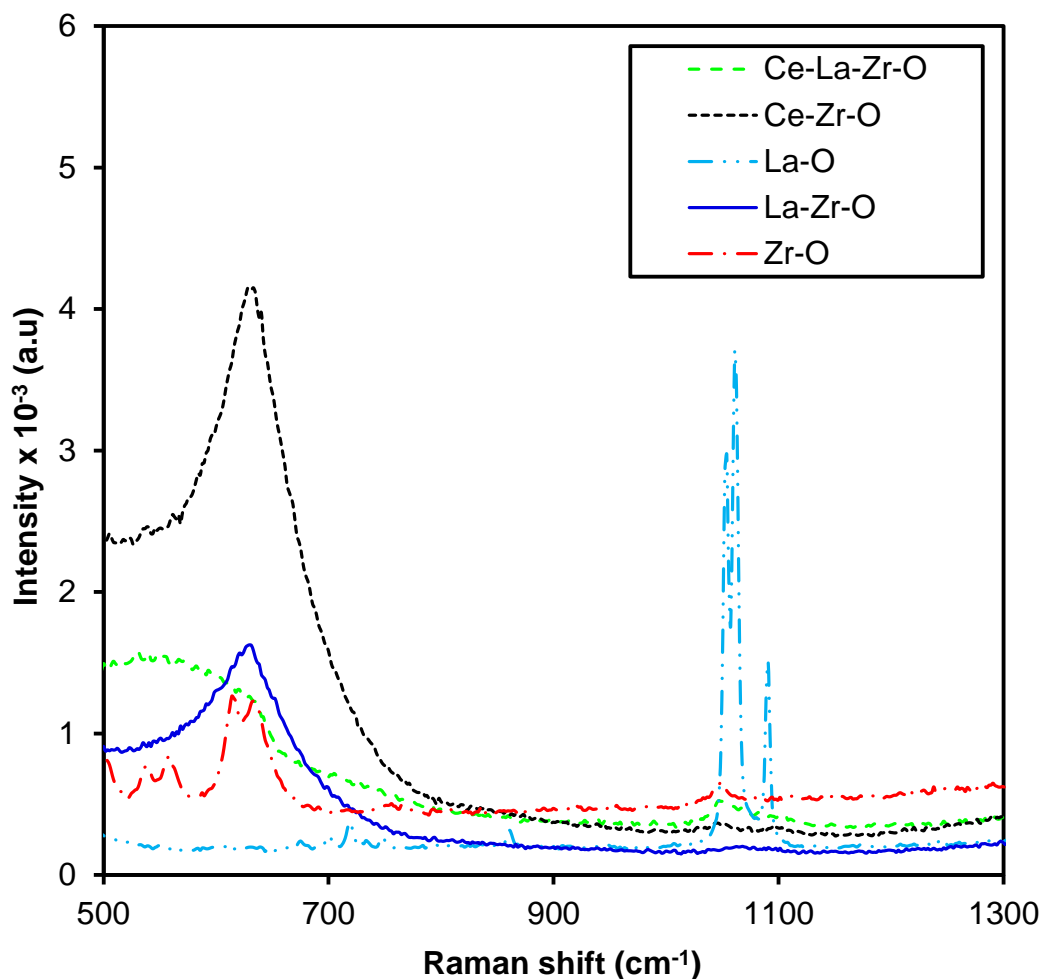
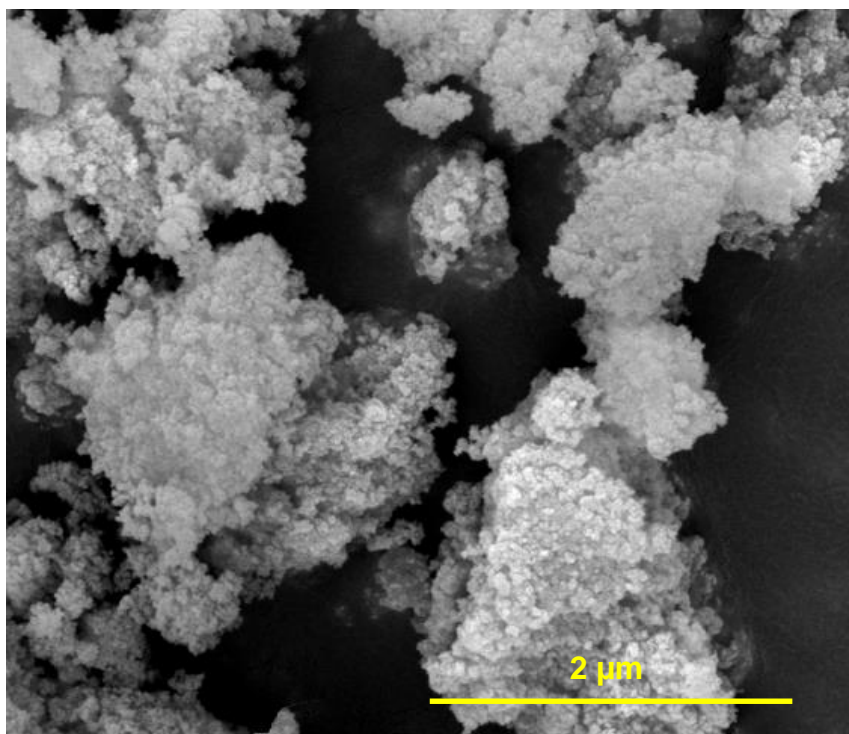


Figure 3.14. Raman spectra of ceria and lanthana doped zirconia (Ce-La-Zr-O), ceria doped zirconia (Ce-Zr-O), lanthanum oxide (La-O), lanthana doped zirconia (La-Zr-O) and zirconium oxide (Zr-O) catalysts.

### 3.7.8. Scanning Electron Microscopic (SEM) Analysis

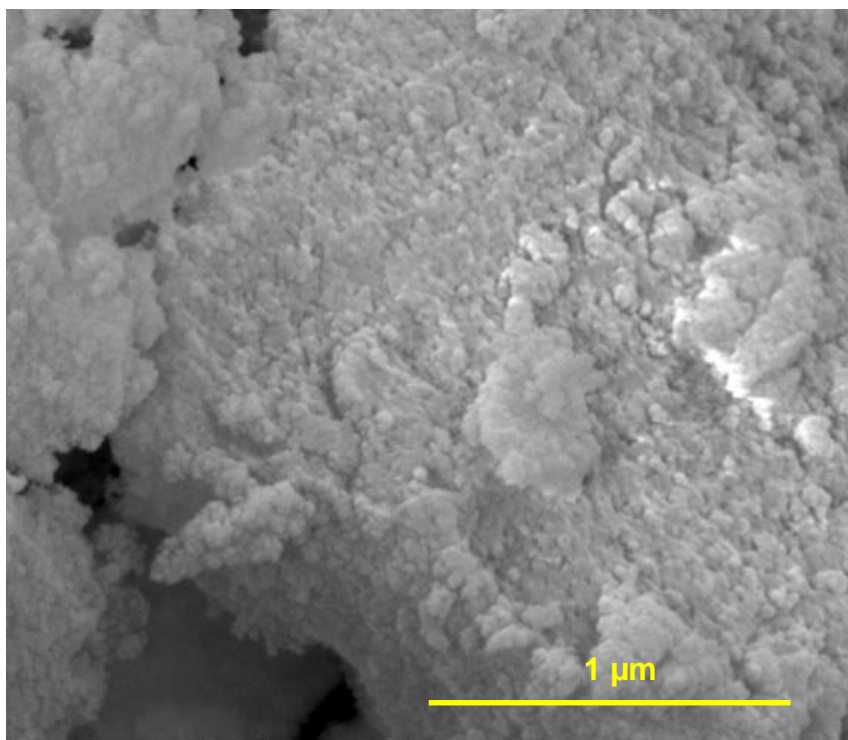
SEM analysis of commercially available catalysts including Ce-La-Zr-O, Ce-Zr-O, La-Zr-O, La-O and Zr-O were carried out using FEI Inspect F and Quanta 3D FEG with a gold plated sample holder. The surface topographic images of the catalysts are presented in Figures 3.15–3.19. Figure 3.15 depicts Ce-La-Zr-O image with well dispersed circular smooth surface, whereas Figure 3.16 represents Ce-Zr-O image with homogeneously aggregated irregular shape surface. Figure 3.17 shows La-O catalyst with rectangular grain-like surface. The SEM image of La-Zr-

O catalyst shown in Figure 3.18 has aggregated circular smooth surface, while Figure 3.19 shows Zr-O catalyst with irregular grain like surface. Figure 3.15 – 3.19 clearly depicts that the incorporation of the dopants (lanthana and ceria) have strong influence on the morphology of the catalyst.

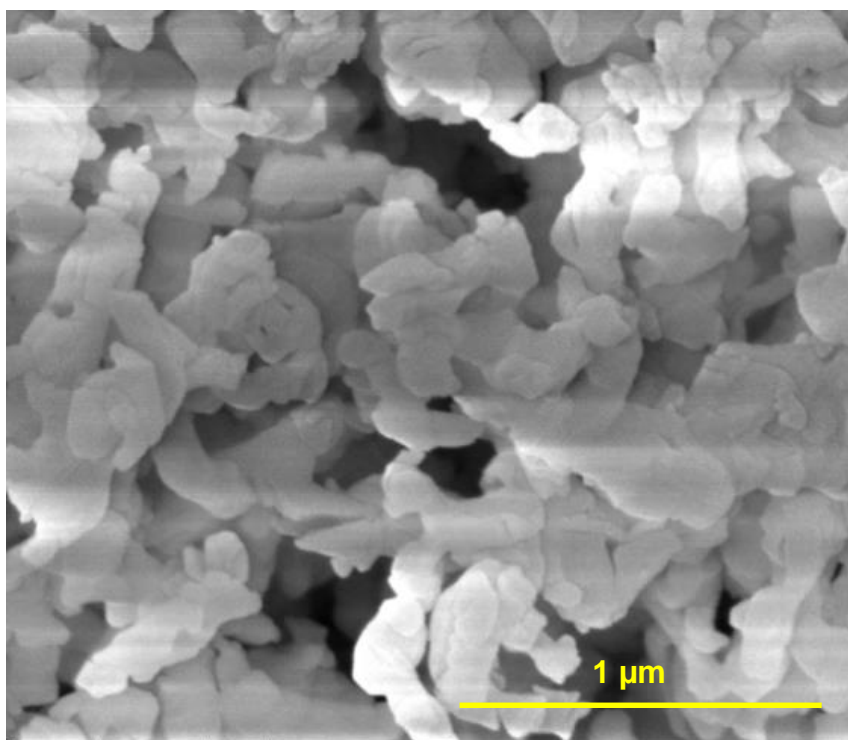


**Figure 3.15.** Scanning electron microscopy (SEM) image of ceria and lanthana doped zirconia (Ce-La-Zr-O) catalyst.





**Figure 3.16.** Scanning electron microscopy (SEM) image of ceria doped zirconia (Ce-Zr-O) catalyst.



**Figure 3.17.** Scanning electron microscopy (SEM) image of lanthana (La-O) catalyst.

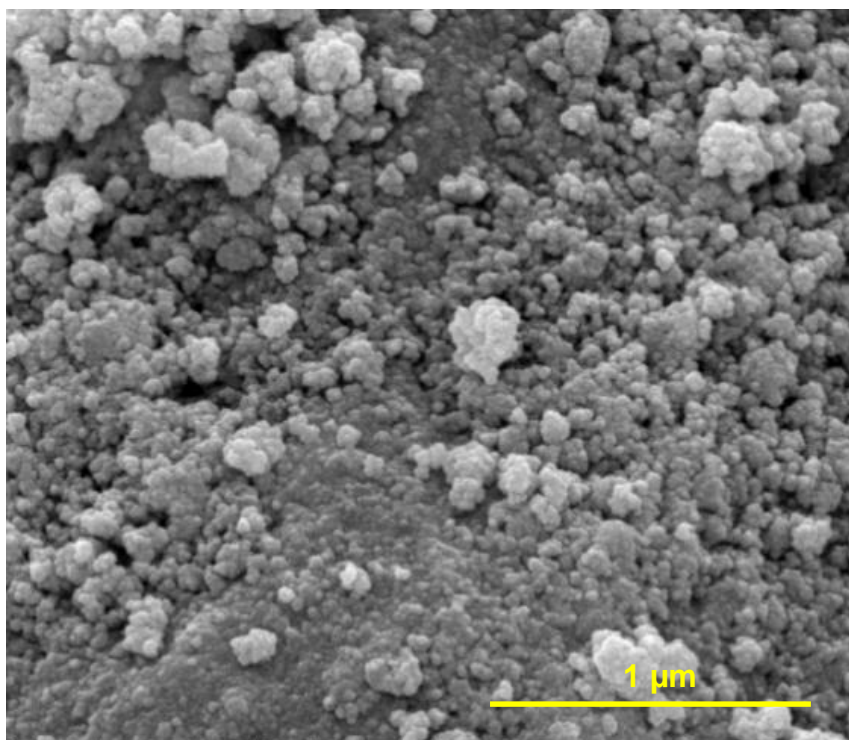
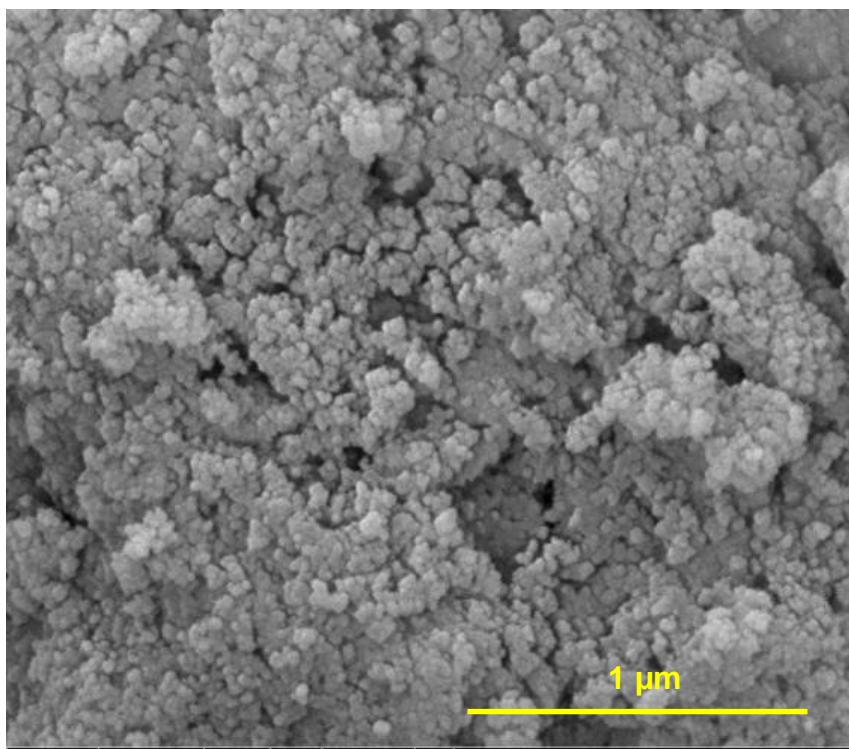


Figure 3.18. Scanning electron microscopy (SEM) image of lanthana doped zirconia (La-Zr-O) catalyst.



**Figure 3.19.** Scanning electron microscopy (SEM) image of zirconia (Zr-O) catalyst.

### 3.7.9. Transmission Electron Microscopy (TEM) Analysis

Particle size and morphology of as-prepared (AP) and the corresponding heat-treated graphene nanocomposite catalysts (HT-500, HT-700 and HT-900) were investigated using a JEOL 2100FCs with a Schottky Field Emission Gun transmission electron microscope (200 kV accelerating voltage). Samples were collected on carbon-coated copper grids (Holey Carbon Film, 300 mesh Cu, Agar Scientific, Essex, UK) after being briefly dispersed ultrasonically in water. TEM images of GO, AP, HT-500, HT-700 and HT-900 are shown in Figures 3.20–3.24 and the mean particle size values are given in Table 3.2. TEM image of GO showing sheet-like surface (Figure 3.20) and images of as-prepared Ce-La-Zr-GO nanocomposite synthesised using CHFS route (sample labelled as “AP”) revealed uniform particles exhibiting a mean particle size of  $5.78 \pm 1.56$  nm is presented in Figure 3.21. The TEM images for the corresponding heat-treated sample at 773 K (labelled as “HT-500”, Figure 3.22) showed similar particle size with a mean particle size of  $5.44 \pm 1.39$  nm. By contrast, the sample heat-treated at 973 K (labelled as “HT-700”, Figure 3.23) revealed an increase in particle size (mean particle size of  $8.88 \pm 1.72$  nm), which further increased when the catalyst was heat-treated at 1173 K (labelled as “HT-900”, Figure 3.24) and exhibited the largest mean crystallite size of  $26.0 \pm 8.5$  nm.

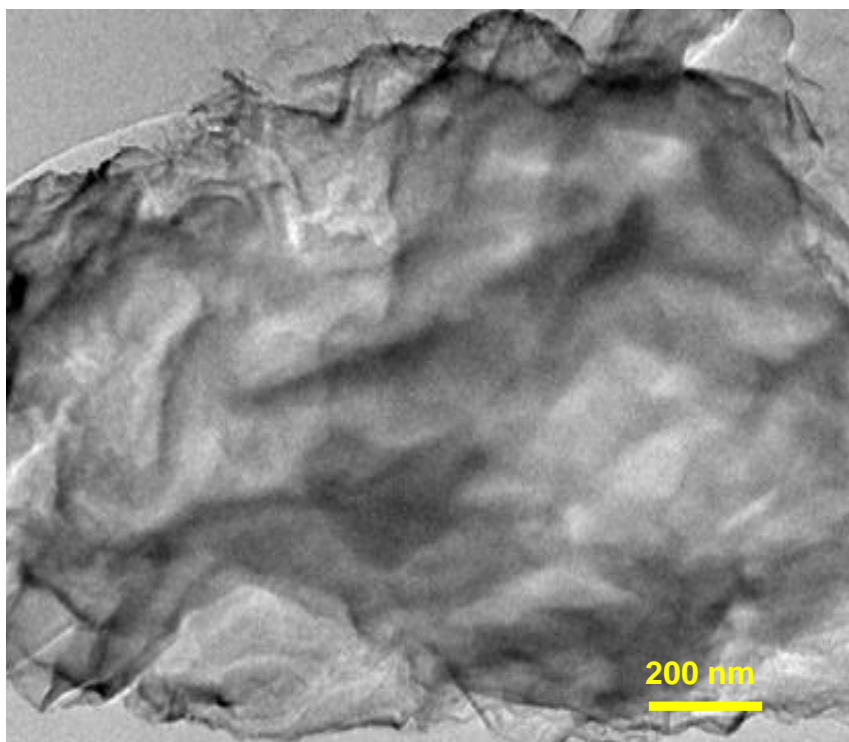
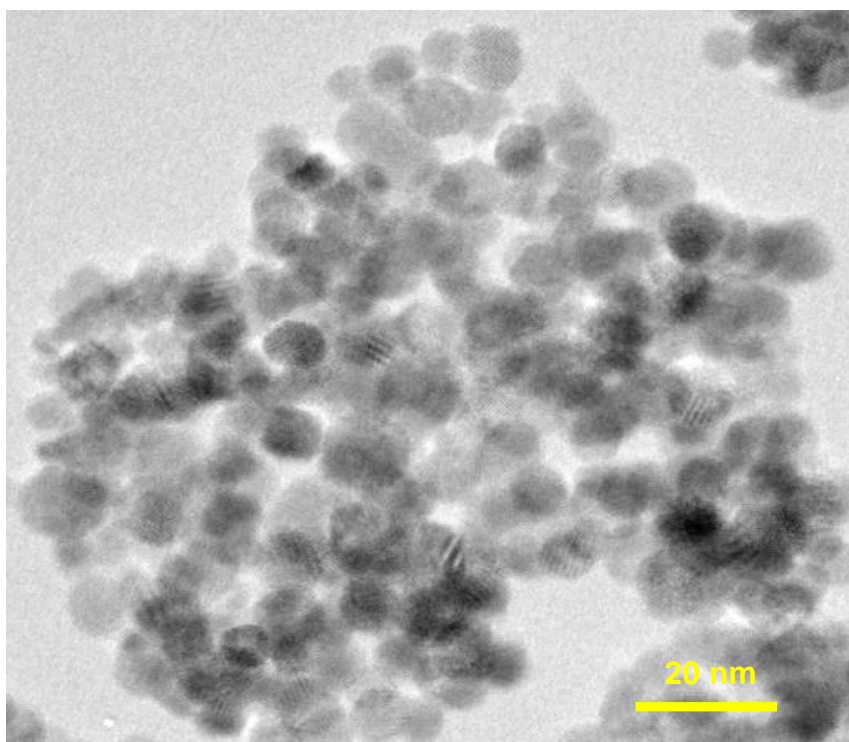


Figure 3.20. Transmission electron microscopy (TEM) image of graphene oxide (GO).



**Figure 3.21.** Transmission electron microscopy (TEM) image of as-prepared Ce-La-Zr-GO (AP) catalyst.



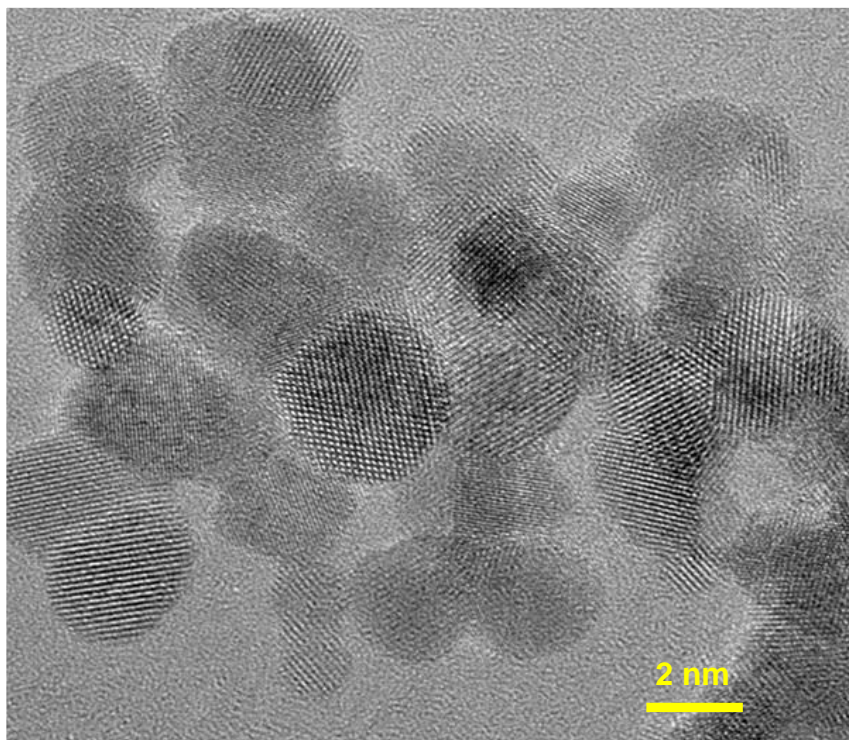


Figure 3.22. Transmission electron microscopy (TEM) image of HT-500 catalyst.

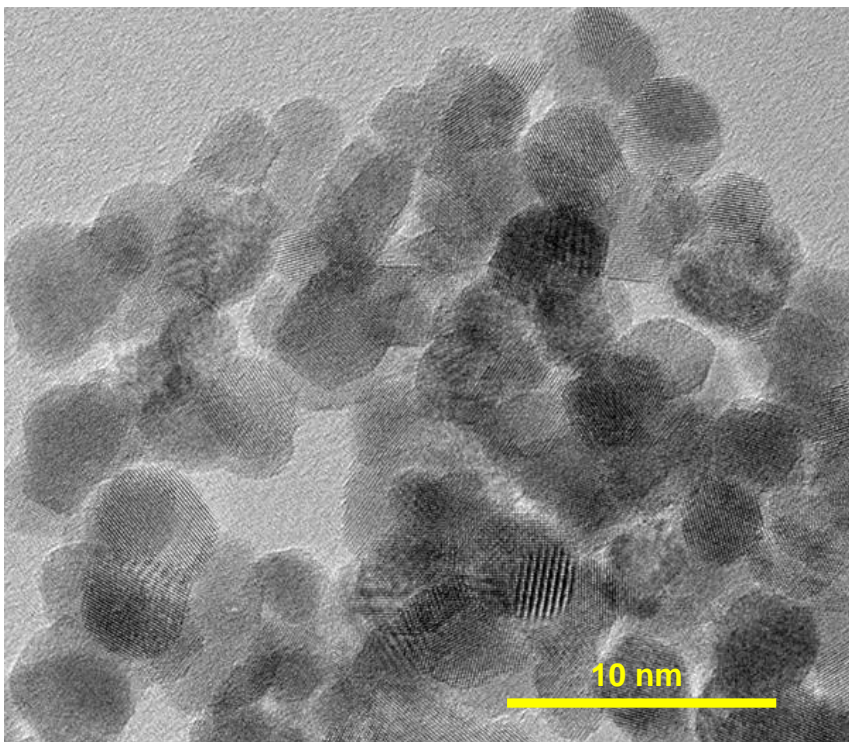
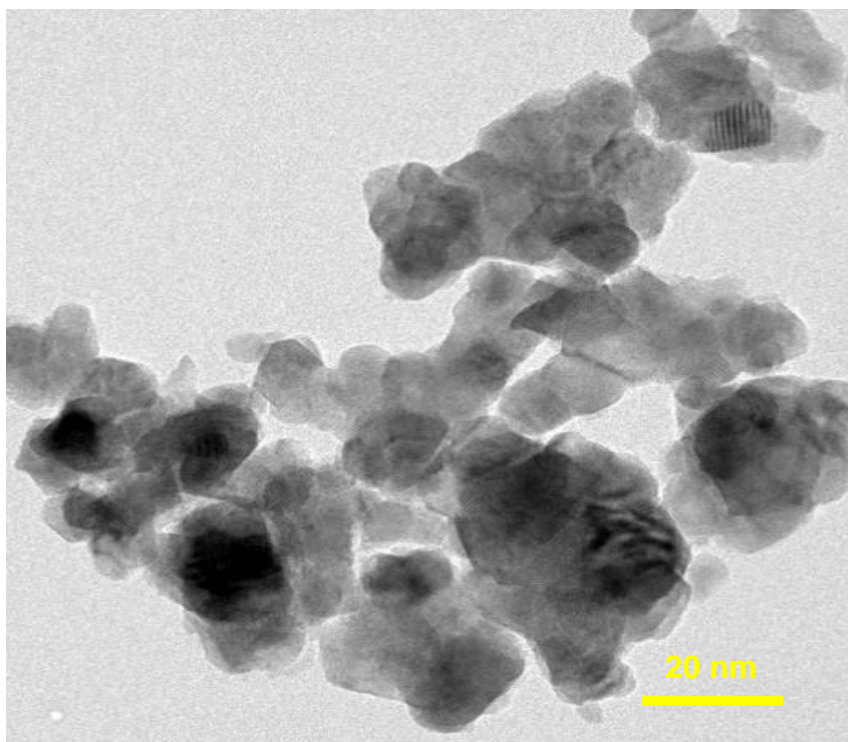


Figure 3.23. Transmission electron microscopy (TEM) image of HT-700 catalyst.



**Figure 3.24.** Transmission electron microscopy (TEM) image of HT-900 catalyst.

### 3.8. Conclusions

Several inorganic nanocomposite catalysts were successfully prepared using a continuous hydrothermal flow synthesis (CHFS) reactor. Graphene oxide (GO) was prepared using an improved method by Hummer and Offerman (1958). The characterisation of various catalysts including commercially available catalysts, as-prepared (Ce-La-Zr-O) catalyst prepared *via* a CHFS reactor and the corresponding heat-treated HT-500, HT-700 and HT-900 catalysts, and GO was carried out successfully to reveal useful information about the active sites relevant to catalytic processes. All the catalysts are in mesoporous range (2–50 nm). GO gave largest surface area of  $124 \text{ m}^2 \text{ g}^{-1}$ , Ce-La-Zr-O catalyst showed surface area of  $55 \text{ m}^2 \text{ g}^{-1}$  and HT-500 catalyst synthesized *via* a CHFS and heat-treated at 773 K showed specific surface area of  $92 \text{ m}^2 \text{ g}^{-1}$ .

## ***CHAPTER 4***

# ***EXPERIMENTAL METHODS FOR CYCLIC ORGANIC CARBONATES SYNTHESSES***

## 4. EXPERIMENTAL METHODS FOR CYCLIC ORGANIC CARBONATES SYNTHESSES

### 4.1. Introduction

The syntheses of cyclic carbonates investigation through addition reaction of various epoxides and carbon dioxide (CO<sub>2</sub>) using heterogeneous catalysts have been carried out in a high pressure reactor at a wide range of experimental conditions. A detailed description of experimental methods, analytical method, determination of cyclic carbonate efficiency and general proposed reaction mechanism for the addition of epoxides and carbon dioxide (CO<sub>2</sub>) in the presence of heterogeneous catalyst are discussed.

### 4.2. Experimental Methods

Cycloaddition reaction of various epoxides and CO<sub>2</sub> are carried out in a high pressure reactor in the presence of several heterogeneous catalysts. Shimadzu GC-2014 gas chromatograph (GC) was used to analyse the reaction mixture and internal standardisation method was used for quantification of all the components present in the reaction mixture.

#### 4.2.1. Materials and Chemicals

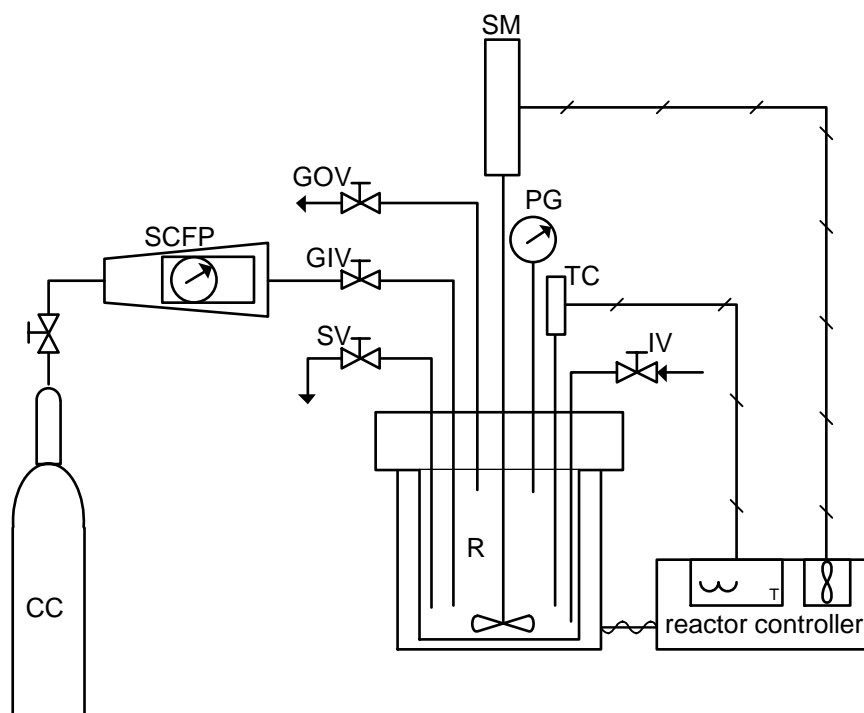
Acetone (99%), *iso*-octane (99.8%), propylene oxide (99.5%), propylene carbonate (98%) and epichlorohydrin (99%) were purchased from Fisher Scientific UK Ltd. Methanol (99%), 1,2-epoxybutane (≥99%), 4-ethyl-1,3-dioxolan-2-one (99%), (chloromethyl)ethylene carbonate (99%), 4-vinyl-1-cyclohexene epoxide (98%), 2-ethyl-4-methyl-1,3-dioxolane (99%) and *n*-Pentane (99.8%) were procured from Sigma-Aldrich Co. LLC, UK. The purity of all the chemicals was verified by gas chromatography (GC) analysis. All chemicals were used without further purification. High purity (99.9%) helium gas and liquid CO<sub>2</sub> (99.9%) cylinder equipped with a dip tube was purchased from BOC Ltd., UK. Supercritical fluid (SCF) pump (model: SFT-10) was procured from Analytix Ltd., UK. A Parr high pressure stainless steel autoclave reactor (model: 5500) of 100 mL and



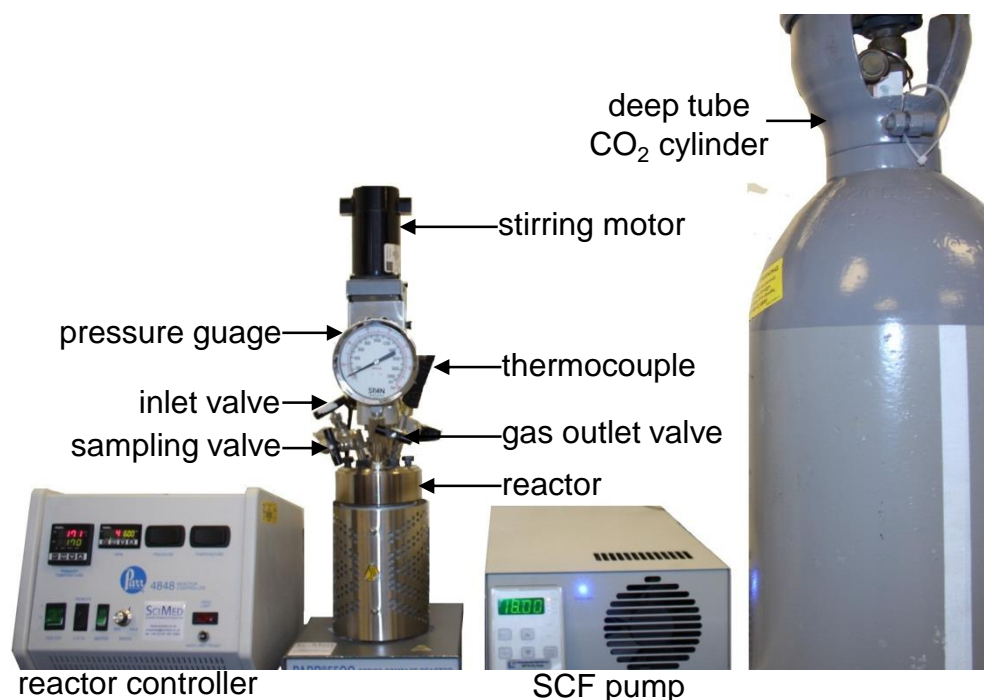
(model 4590) of 25 mL capacity equipped with a reactor controller (model: 4848) was purchased from SCIMED (Scientific and Medical Products Ltd.), UK. Risk assessment (RA) for batch reactor experiments were carried out before conducting the experiments and the RA records are attached in Appendix D.

### 4.2.2. Experimental Procedure

Cycloaddition reactions of epoxides such propylene oxide (PO), 1,2-epoxybutane (BO), epichlorohydrin (ECH) and 4-vinyl-1-cyclohexene epoxide (VCHE), and CO<sub>2</sub> were carried out in a mechanically stirred high pressure reactor (model 5500 Parr Instrument Company, USA) equipped with a pressure gauge, stirrer, thermocouple (type J) and a heating mantle and controller (model 4848). The schematic and image of the experimental set-up for organic carbonates syntheses using high pressure reactor are shown in Figures 4.1 and 4.2, respectively. The gas inlet valve at the top of the reactor was connected to a liquid CO<sub>2</sub> cylinder *via* supercritical fluid (SCF) pump (model SFT-10, Analytix Ltd., U.K) that allows liquid CO<sub>2</sub> into the reactor at a desired rate. In a typical experiment, the reactor was initially charged with specific amount of catalyst and the limiting reactant, epoxide. The reactor was then heated to the required temperature and continuously stirred. Once the desired temperature was achieved, a known amount of liquid CO<sub>2</sub> was fed to the high pressure reactor *via* SCF pump. The time at which the liquid CO<sub>2</sub> was charged into the reactor was taken as zero time ( $t = 0$ ) and the reaction mixture was left stirring for a desired period of time. After the reaction, the reactor was cooled down to room temperature using an ice bath, depressurized and then the reaction mixture was filtered. The catalyst was separated, washed with acetone and dried in a vacuum oven. The product obtained from the filtered reaction mixture was then analysed using gas chromatography (GC).



**Figure 4.1.** Schematic representation of the experimental set-up for organic carbonate synthesis using a Parr high pressure reactor. Key: CC = dip tube CO<sub>2</sub> cylinder, SCFP = supercritical fluid pump, GOV = gas outlet valve, GIV = gas inlet valve, SV = sampling valve, R = reactor, IV = inlet valve, TC = thermocouple, PG = pressure guage, SM = stirring motor.



**Figure 4.2.** Image of the experimental set-up for organic carbonate synthesis using a Parr high pressure reactor.

#### 4.2.3. Method of Analysis

Samples collected from the reactor were analyzed by a Shimadzu GC-2014 gas chromatography (GC) equipped with a capillary column of dimensions (30 m x 300  $\mu\text{m}$  x 0.25  $\mu\text{m}$ ) and a flame ionization detector (FID). High purity (99.9%) helium was used as the carrier gas. The flow rate of the helium gas was maintained at 0.95 mL min<sup>-1</sup>. Both the injection and detector temperatures were maintained isothermally. A ramp method was used to distinguish all the components present in the sample mixture. A split ratio of 100:1 and injection volume of 0.5  $\mu\text{L}$  were used as part of the GC ramp method. The sample was injected by an auto sampler.

##### 4.2.3.1. Calibration Curves

Calibration curves were developed to determine the composition of all the components present in the samples collected from batch reactor. An internal standard method was used to develop the calibration curves. To develop calibration curves, a number of samples were prepared with

known concentration and analysed using gas chromatograph. The concentration ratio (CR) and area ratio (AR) of the component were calculated from Equation (4.1) and (4.2), respectively.

$$\text{Concentration ratio (CR)} = \frac{\text{Concentration of component (C}_c\text{)}}{\text{Concentration of internal standard (C}_i\text{)}} \quad (4.1)$$

$$\text{Area ratio (AR)} = \frac{\text{Area of component (A}_c\text{)}}{\text{Area of internal standard (A}_i\text{)}} \quad (4.2)$$

Respond factor (RF) of component is calculated from Equation (4.3).

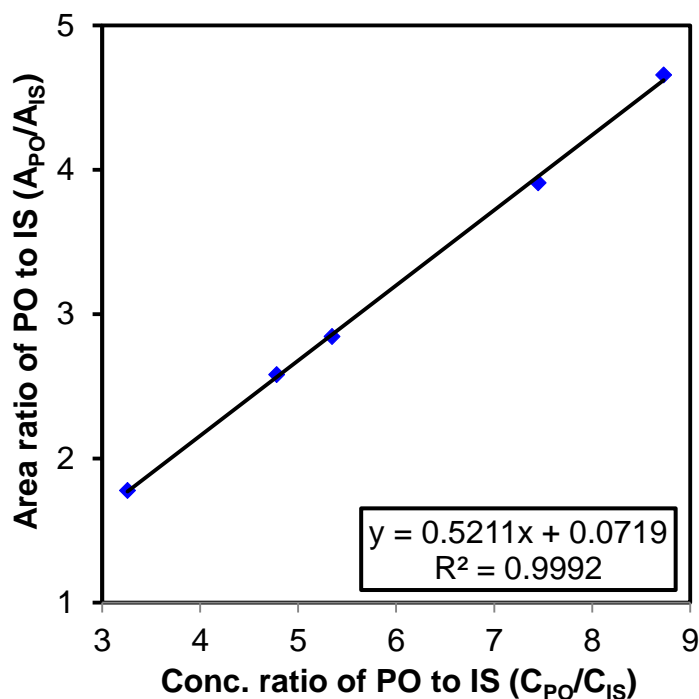
$$\text{Respond factor (RF)} = \frac{\text{Concentration ratio (CR)}}{\text{Area ratio (AR)}} \quad (4.3)$$

Equation (4.3) can be rearranged in the form of equation of straight line ( $y = m x$ ) as shown in Equation (4.4).

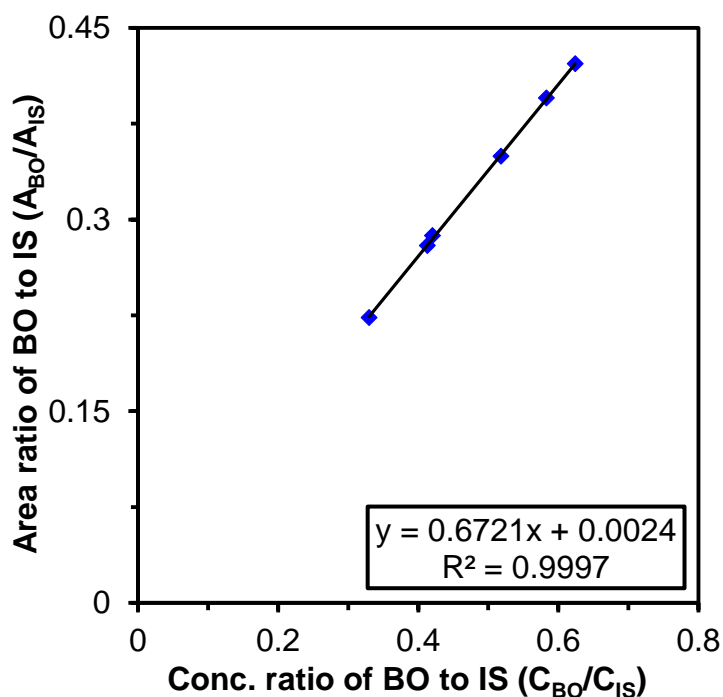
$$\frac{A_c}{A_i} = \text{RF} \frac{C_c}{C_i} \quad (4.4)$$

$y$  is concentration ratio of component in the sample (CR), slope ( $m$ ) is the response factor (RF) determined by the calibration curve of concentration versus area ratio of the component,  $x$  is the area ratio of component in the sample (AR). A plot of concentration ratio versus area ratio of epoxides and cyclic carbonates were plotted for determination of response factor. Once the response factor of individual component was determined, the unknown composition of the samples collected from batch reactor experiments can be determined by Equation 4.4. Figures 4.3 to 4.6 show the calibration curves of propylene oxide, butylene oxide, epichlorohydrin and 4-vinyl-1-cyclohexene epoxide with the response factors of 0.5211, 0.621, 0.7954, and 0.2899, respectively, while Figures 4.7 to 4.10 show the calibration curve of propylene carbonate, butylene carbonate,

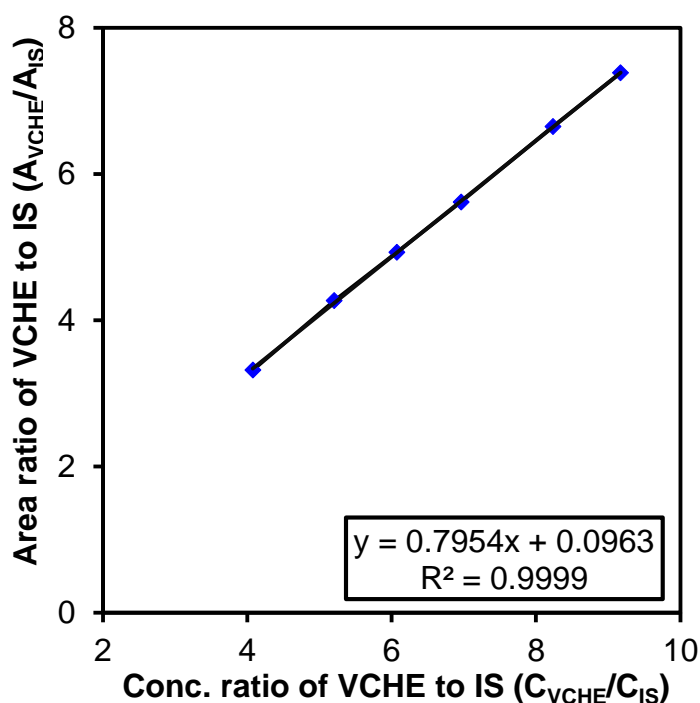
(chloromethyl)ethylene carbonate and 4-vinyl-1-cyclohexene carbonate with the response factor of 0.3031, 0.397, 0.4254 and 0.7319, respectively. Data used in the development of calibration curves for epoxides and the corresponding organic carbonates are shown in the Appendix B.



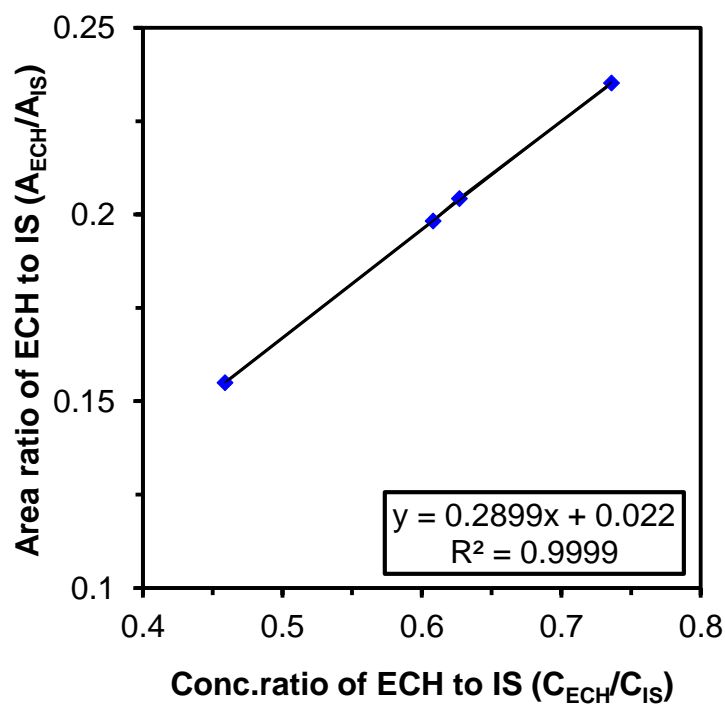
**Figure 4.3.** Calibration curve showing response factor for propylene oxide (PO) using *iso*-octane as an internal standard (IS).



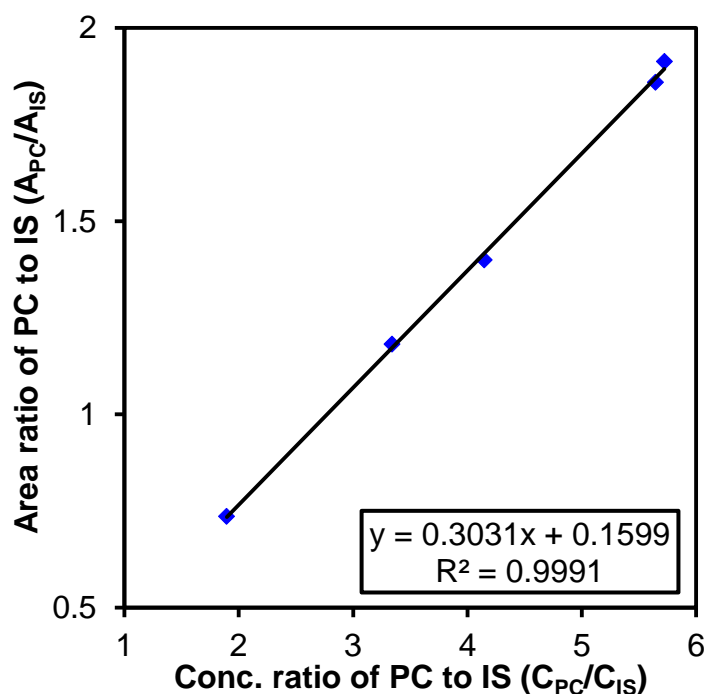
**Figure 4.4.** Calibration curve for response factor determination of butylene oxide (BO) using *iso*-octane as an internal standard (IS).



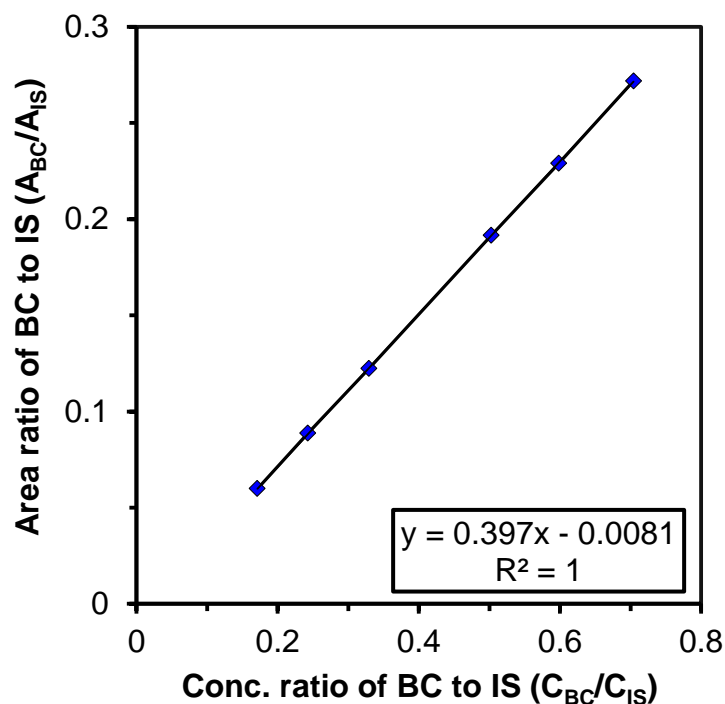
**Figure 4.5.** Calibration curve for response factor determination of 4-vinyl-1-cyclohexene epoxide (VCHE) using *iso*-octane as an internal standard (IS).



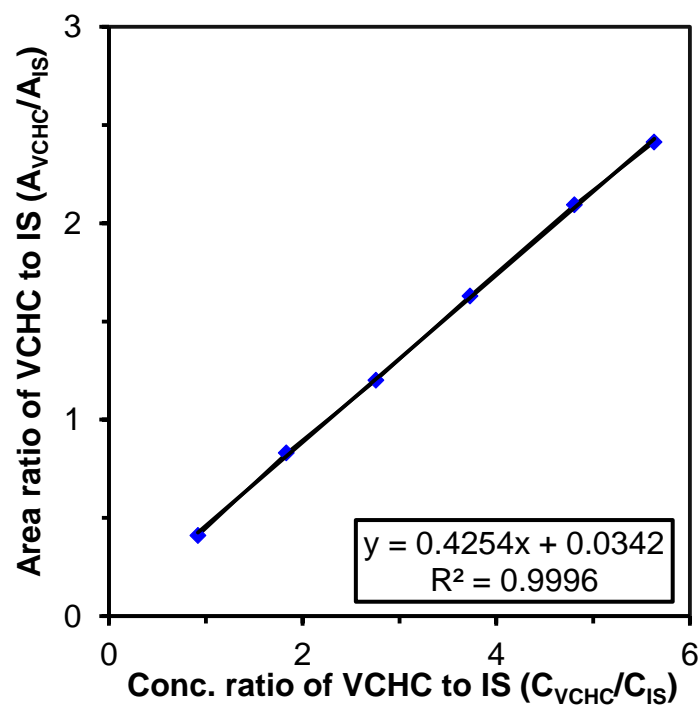
**Figure 4.6.** Calibration curve for response factor determination of epichlorohydrin (ECH) using methanol as an internal standard (IS).



**Figure 4.7.** Calibration curve showing response factor for propylene carbonate (PC) using *iso*-octane as an internal standard (IS).

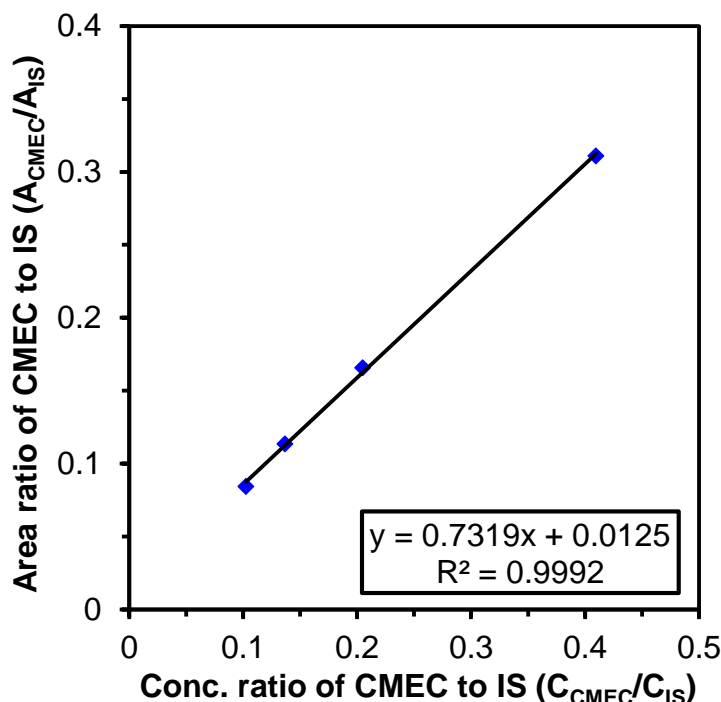


**Figure 4.8.** Calibration curve for response factor determination of butylene carbonate (BC) using *iso*-octane as an internal standard (IS).



**Figure 4.9.** Calibration curve for response factor determination of 4-vinyl-1-cyclohexene carbonate (VCHC) using *iso*-octane as an internal standard (IS).





**Figure 4.10.** Calibration curve for response factor determination of (chloromethyl)ethylene carbonate (CMEC) using methanol as an internal standard (IS).

#### 4.2.3.2. Internal Standardisation

Internal standard method was used for the analysis of the reaction mixture. Internal standardisation technique is defined as a method that combines the sample and standard into one injection. Other methods of analysis include normalisation and external standardisation. The advantages of the internal standardisation technique include clear separation and identification of each components present in the reaction mixture, and the result of each injection is independent of the injection volume. The limitations associated with the internal standardisation method include the technique cannot be used for gaseous samples and there is a need to select a suitable internal standard. *Iso*-Octane was used as an internal standard in the analysis of organic carbonates syntheses which includes propylene carbonate (PC), butylene carbonate (BC) and 4-vinyl-1-cyclohexene carbonate (VCHC) synthesis. Methanol was employed

as internal standard in the synthesis of (chloromethyl)ethylene carbonate (CMEC).

The pre-requisites for an internal standard are:

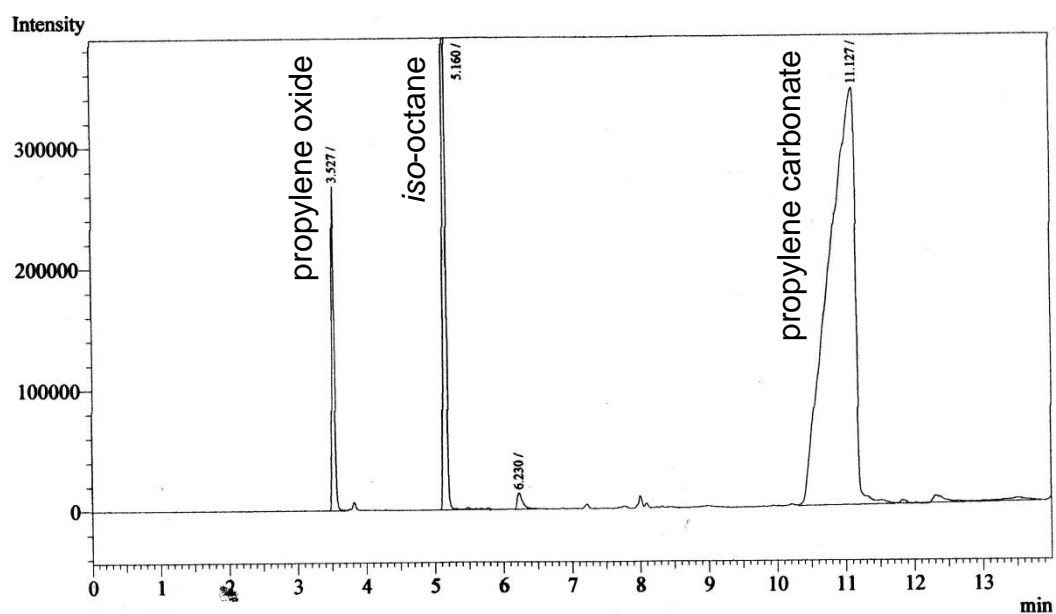
- The internal standard must be miscible with the samples being analysed.
- The internal standard must elute from the column and adequately separated from all samples components i.e. during the GC analysis, the internal standard should give only one peak which must be well resolved from the peaks of the sample components.
- The internal standard must elute as near as possible to the desired components and ideally before the last sample peak so that the analysis time is not increased.
- The internal standard should preferably be similar in functional group type to the component(s) of interest. If such a compound is not readily available, an appropriate hydrocarbon should be substituted.
- The Internal standard must be stable under the required analytical conditions and must not react with any of the components or solvents present in the sample.
- The internal standard must be sufficiently non-volatile to make allowance for storage of standard solutions for significant periods of time.

### 4.2.3.3. Chromatograms

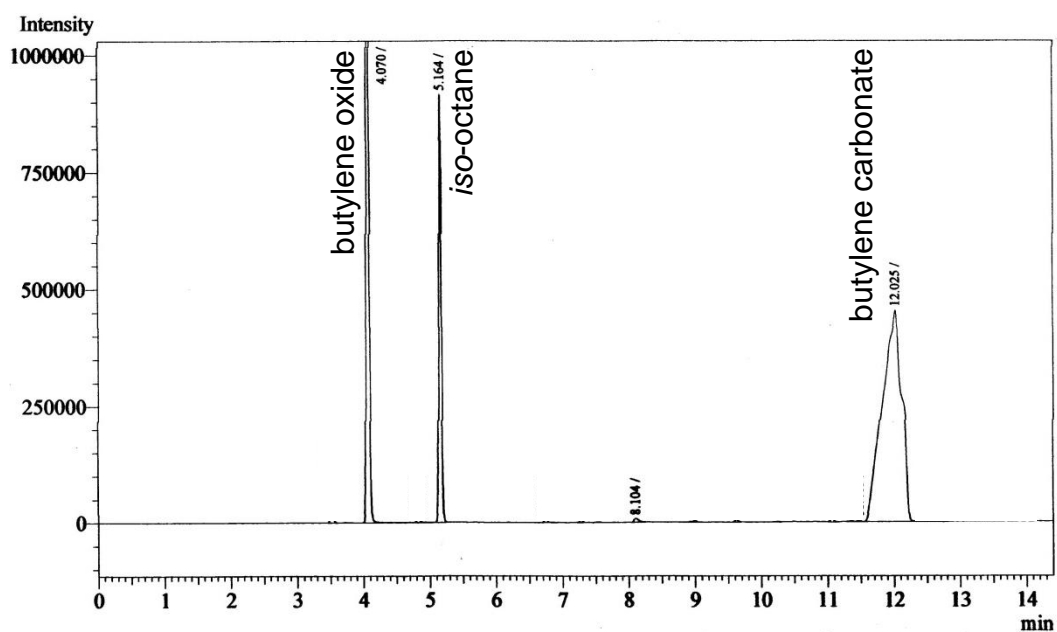
The mixture of internal standard and reaction mixture samples were injected into Shimadzu GC-2014 gas chromatograph. The typical chromatograms of the internal standard and the chemical components present in the reaction mixture obtained from the cycloaddition reaction

of epoxides and CO<sub>2</sub> to produce organic carbonates are presented in Figures 4.11 to 4.14.

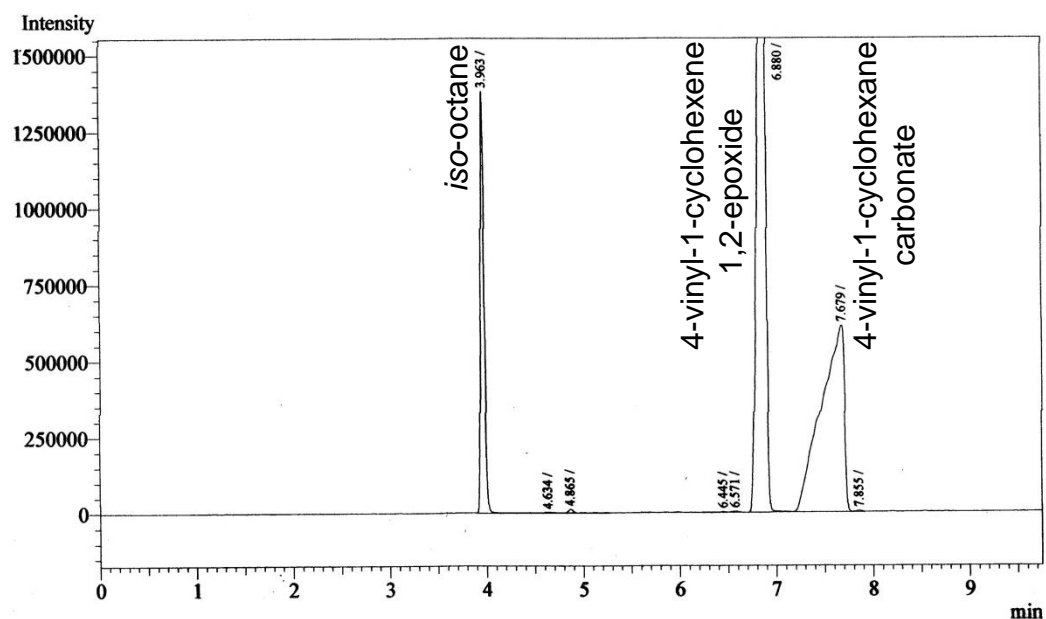
Figure 4.11 revealed a typical chromatogram of the components present in the sample mixture collected from cycloaddition reaction of PO and CO<sub>2</sub> to produce PC. The Shimadzu GC-2014 GC analyses showed that PO peak emerged at a residence time of ~3.5 min followed by *iso*-octane peak at ~5 min and PC peak at ~11 min. The total run time for each sample was ~14 min. Figure 4.12 shows the chromatogram of the components present in the reaction mixture sample from cycloaddition reaction of BO and CO<sub>2</sub> to produce BC. BO peak emerged at a residence time of ~4 min followed by *iso*-Octane peak at ~5.1 min and BC peak at ~12 min. The total run time for each sample was ~14 min. Figure 4.13 illustrated a typical chromatogram of the components present in the sample mixture collected from cycloaddition reaction of VCHE and CO<sub>2</sub> to produce VCHC. *iso*-Octane peak emerged at a residence time of ~ 3.9 min followed by VCHE peak at ~6.9 min and VCHC peak at ~7.7 min. The total run time for each sample was ~10 min. Figure 4.14 provides a typical chromatogram of the components present in the reaction mixture from cycloaddition reaction of ECH and CO<sub>2</sub> to produce CMEC. Methanol (internal standard) peak emerged at a residence time of ~3.3 min followed by ECH peak at ~5.7 min and CMEC peak at ~14.6 min. The total run time for each sample was ~17 min.



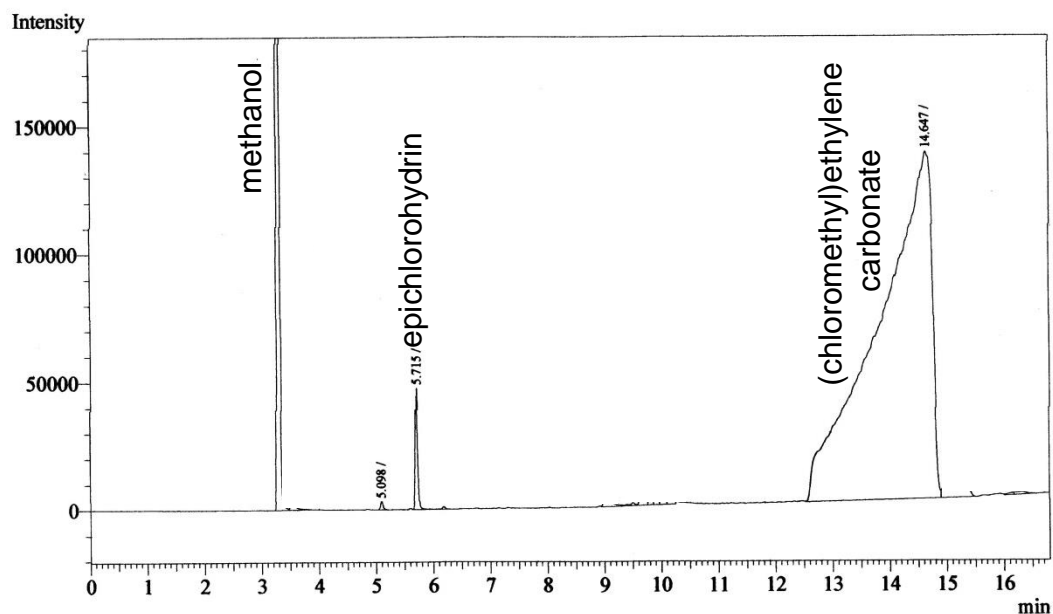
**Figure 4.11.** Chromatogram of the components present in the reaction mixture of propylene carbonate (PC) synthesis.



**Figure 4.12.** Chromatogram of the components present in the reaction mixture of butylene carbonate (BC) synthesis.



**Figure 4.13.** Chromatogram of the components present in the reaction mixture of 4-vinyl-1-cyclohexene carbonate (VCHC) synthesis.



**Figure 4.14.** Chromatogram of the components present in the reaction mixture of (chloromethyl)ethylene carbonate (CMEC) synthesis.

#### 4.2.3.4. Determination of Conversion of Epoxides, Selectivity and Yield of Organic Carbonates

The percentage (%) conversion (X) of epoxide was calculated as the ratio of epoxide reacted to the amount of epoxide charged (Equation 4.5). The percentage (%) yield (Y) was calculated as the ratio of organic carbonate formed to the amount of epoxide charged (Equation 4.6), and percentage (%) selectivity (S) was calculated as the ratio of yield (Y) to conversion (X) (Equation 4.7). In each equation  $n$  represents the amount in terms of mol.

$$\text{Percentage conversion (X)} = \frac{n_{AO} - n_A}{n_{AO}} \times 100 \quad (4.5)$$

$$\text{Percentage yield (Y)} = \frac{n_C}{n_{AO}} \times 100 \quad (4.6)$$

$$\text{Percentage selectivity (S)} = \frac{Y}{X} \times 100 \quad (4.7)$$

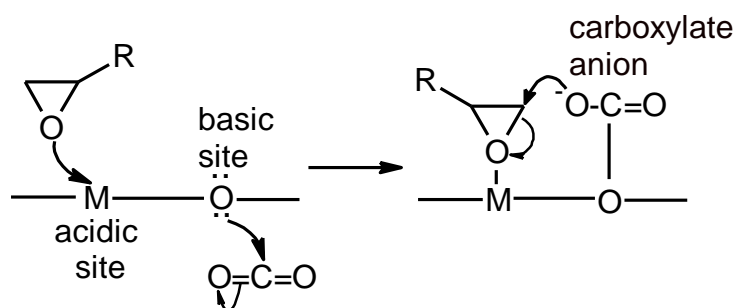
Where  $n_{AO}$  is the mole of epoxide charged into the reactor,  $n_A$  is the mole of epoxide after reaction and  $n_C$  is the mole of organic carbonate formed.

#### 4.3. Proposed Reaction Mechanism for Cyclic Organic Carbonates Syntheses

The cycloaddition reaction of epoxides and  $\text{CO}_2$  in the presence of heterogeneous catalyst produces a value added product, i.e., organic carbonates along with other side products. Step 4.1 to 4.3 of the proposed reaction mechanism is shown in Figures 4.15 to 4.17. In the proposed mechanism, R is an alkyl group, M represents a metal atom consisting of Lewis acid site and O represents an oxygen atom consisting of Lewis basic site. Cycloaddition reaction was initiated by adsorption of  $\text{CO}_2$  on the basic site of the metal oxide catalyst to form a carboxylate anion and epoxide was activated by adsorption on the acidic site. The carbon atom of epoxide is attacked by a carboxylate anion that leads to the ring

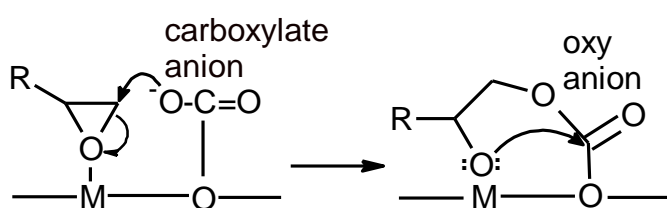
opening of epoxide to form an oxy-anion specie. Dissociation of metal oxide (catalyst) from the oxy-anion specie leads to a ring closure and desorption of organic carbonate as a product (Adeleye *et al.*, 2014; Dai *et al.*, 2009; Yamaguchi *et al.*, 1999). The side products associated with cycloaddition reaction of CO<sub>2</sub> and epoxide includes isomers of epoxide such as acetone and propionaldehyde, and dimers of epoxide including 2-ethyl-4-methyl-1, 3-dioxolane and their derivatives (Fasi *et al.*, 2001; Wang *et al.*, 2007).

Reaction mechanism step 4.1.



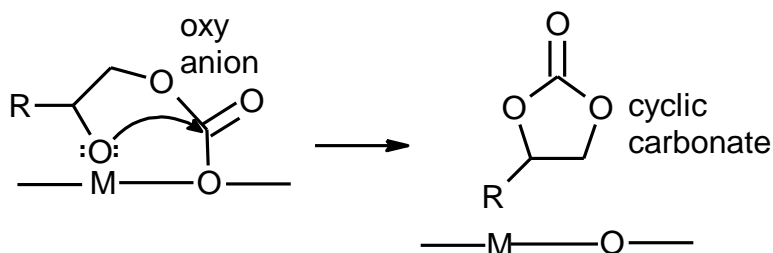
**Figure 4.15.** Initiation by adsorption of epoxide and CO<sub>2</sub> on metal oxide catalysts.

Reaction mechanism step 4.2.



**Figure 4.16.** Ring opening of epoxide to form oxy-anion specie.

Reaction mechanism step 4.3.



**Figure 4.17.** Ring closure and desorption of cyclic organic carbonate.

In all above reaction mechanism steps, R is an alkyl group, MO represents metal oxide catalyst, where M is a metal atom and O is an oxygen atom.

#### 4.4. Conclusions

Cycloaddition reaction of epoxides and CO<sub>2</sub> to produce cyclic organic carbonates were successfully carried out in a Parr high pressure reactor. The reaction mixture samples collected from the reactor were systematically analysed using a Shimadzu GC-2014 gas chromatography (GC). An internal standard method was used to develop the calibration curves for quantification of the components present in the reaction mixture.



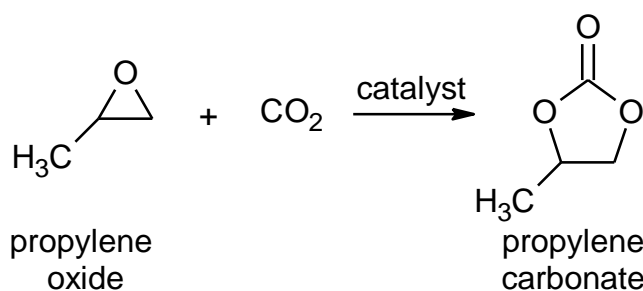
## ***CHAPTER 5***

# ***HETEROGENEOUS CATALYSTS FOR CONVERSION OF CARBON DIOXIDE TO PROPYLENE CARBONATE***

## 5. HETEROGENEOUS CATALYSTS FOR CONVERSION OF CARBON DIOXIDE TO PROPYLENE CARBONATE

### 5.1. Introduction

Several heterogeneous catalysts have been investigated for solvent-free synthesis of propylene carbonate (PC) from addition reaction of propylene oxide (PO) and carbon dioxide (CO<sub>2</sub>) as shown in Figure 5.1. Batch cycloaddition reaction of PC and CO<sub>2</sub> has been conducted in a high pressure reactor. The effect of various parameters that could influence the conversion of PO, selectivity and yield of PC such as catalyst types, catalyst loading, CO<sub>2</sub> pressure, reaction temperature and reaction time has been studied to find the optimum conditions and the best preferred catalyst for the reaction.



**Figure 5.1.** Reaction scheme of propylene carbonate synthesis from cycloaddition reaction of propylene oxide and carbon dioxide.

### 5.2. Experimental Methods

#### 5.2.1. Chemicals

Acetone (99%), *iso*-octane (99.8%), propylene oxide (99.5%), propylene carbonate (98%) were purchased from Fisher Scientific UK Ltd. 2-ethyl-4-methyl-1, 3-dioxolane (99%) (w/w) and *n*-Pentane (99.8%) (w/w) were procured from Sigma-Aldrich Co. LLC. The purity of all chemicals was verified by gas chromatography (GC) analysis. These chemicals were used without further purification.

### 5.2.2. Catalysts

Several heterogeneous catalysts includes commercially available catalysts such as ceria, lanthana doped zirconia (abbreviated as Ce-La-Zr-O), ceria doped zirconia (abbreviated as Ce-Zr-O), lanthana doped zirconia (abbreviated as La-Zr-O), lanthana (abbreviated as La-O), magnesium aluminium oxide (abbreviated as Mg-Al-O), magnesium oxide (abbreviated as Mg-O) and zirconia (abbreviated as Zr-O), and catalysts prepared using a continuous hydrothermal flow synthesis (CHFS) reactor including ceria, lanthana doped zirconia (abbreviated as Ce-La-Zr-O), ceria, lanthana and zirconia graphene oxide (abbreviated as Ce-La-Zr-GO), ceria and zirconia graphene oxide (abbreviated as Ce-Zr-GO), ceria doped zirconia (abbreviated as Ce-Zr-O), graphene oxide (GO), lanthana (labelled as La-O) and zirconia (labelled as Zr-O) were used without further purification.

### 5.2.3. Experimental Procedure

Cycloaddition reaction of PO and CO<sub>2</sub> was carried out in a mechanically stirred Parr high pressure reactor. The reactor was equipped with a pressure gauge and a thermocouple that monitor the pressure and temperature inside the reactor, respectively at any given time. The heating of the reactor was provided by an aluminum cylindrical heater that is connected to the controller unit. The gas inlet valve at the top of the reactor was connected to a liquid CO<sub>2</sub> cylinder *via* a supercritical fluid (SCF) pump that allows liquid CO<sub>2</sub> into the reactor at a desired rate.

During any given experiment, the reactor was charged with specific amount of catalyst and the limiting reactant, i.e., PO. The mechanical stirrer was started at a known stirrer speed and the reactor was heated to the desired temperature. Once the desired temperature was achieved, a known amount of liquid CO<sub>2</sub> was fed to the high pressure reactor *via* a supercritical fluid (SCF) pump. The time at which the liquid CO<sub>2</sub> was charged into the reactor was taken as zero time, i.e.,  $t = 0$  and the reaction

mixture was left for a desired period. Once the experiment was completed, stirring and heating of the reactor were switched off, the reactor was cooled in an ice bath and the excess CO<sub>2</sub> present in the reactor was vented out. The reaction mixture was filtered and the catalyst was separated, washed with acetone and dried in a vacuum oven.

### 5.2.4. Methods of Analysis for Propylene Carbonate Synthesis

The sample collected from the reaction mixture of cycloaddition reaction of propylene oxide (PO) and CO<sub>2</sub> to produce propylene carbonate (PC) was analysed using a Shimadzu GC-2014 gas chromatograph (GC). The initial column temperature was maintained at 323 K and the sample was injected by an auto sampler. The column temperature was set to hold at 323 K for 5 min after sample injection. The column temperature was increased to 523 K at the rate of 25°C min<sup>-1</sup>. The total run time for each sample was ~14 min. *n*-Pentane was used as a solvent to rinse the injection needle after the sample injection. The subsequent sample runs were started when the column temperature was cooled back to 323 K. Internal standard method was used for quantification of all the components present in the sample mixture and *iso*-Octane was used as an internal standard. The experimental error for batch studies conducted in a high pressure reactor using GC technique was in the range of ±3%.

### 5.3. Synthesis of Propylene Carbonate using Commercially Available Heterogeneous Catalysts

Several commercial available heterogeneous catalysts such as Ce-La-Zr-O, Ce-Zr-O, La-O, La-Zr-O and Zr-O have been investigated for solvent-free synthesis of propylene carbonate (PC) for cycloaddition reaction of propylene oxide (PO) and carbon dioxide (CO<sub>2</sub>) in a high pressure reactor.

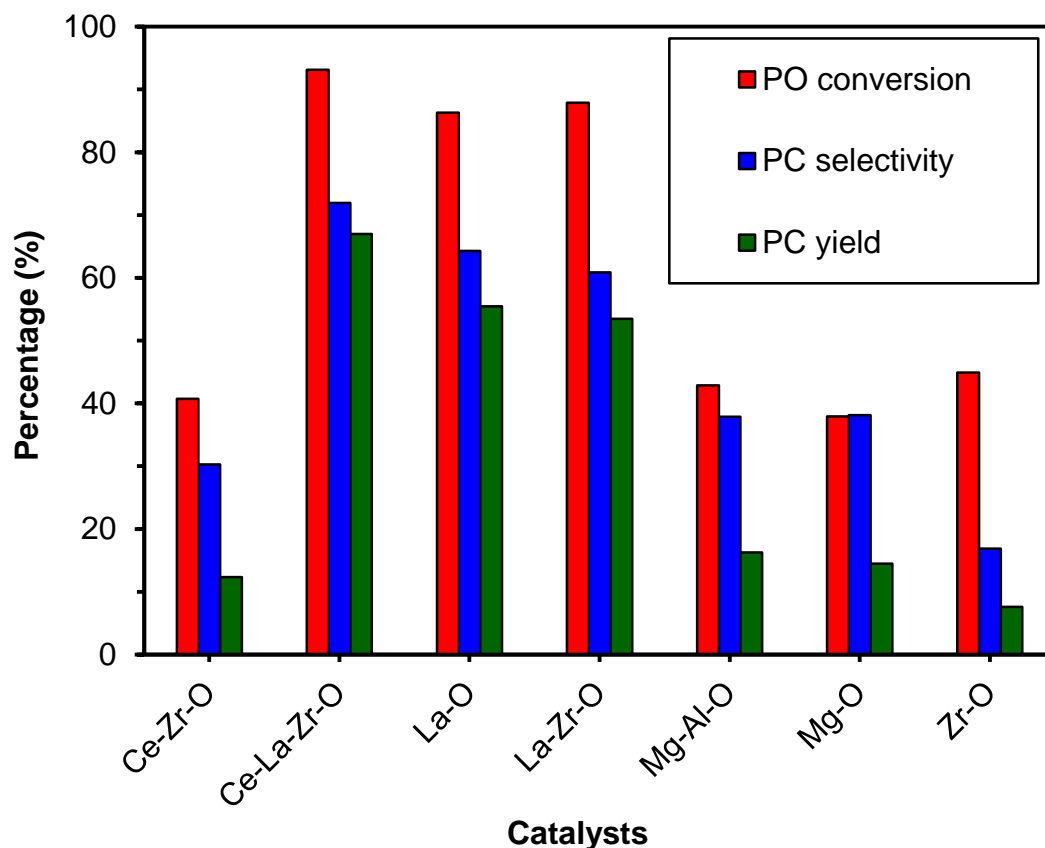
### 5.3.1. Results and Discussions

The effect of various parameters such as catalyst types, catalyst loading, CO<sub>2</sub> pressure, reaction temperature and reaction time has been studied to find the optimum conditions and the best preferred catalyst for the reaction.

#### 5.3.1.1. Effect of Different Catalysts

Several commercially available heterogeneous catalysts were tested in order to study the catalytic activity and selectivity for the production of PC from the reaction of PO and CO<sub>2</sub> using a high pressure reactor. Figure 5.2 shows the effect of different catalysts which including Ce-La-Zr-O, Ce-Zr-O, La-O, La-Zr-O, Mg-Al-O, Mg-O and Zr-O on the conversion of PO and on the yield and selectivity of PC. It can be seen from Figure 5.2 that Ce-La-Zr-O catalyst gave highest conversion of PO (~92%) and highest PC yield (66%) and selectivity (72%). The presence of La<sub>2</sub>O<sub>3</sub> has a significant effect on the catalytic activity of Ce-La-Zr-O catalyst for the cycloaddition reaction of PO and CO<sub>2</sub>. Similarly, La-O catalyst exhibits PO conversion of ~86% and PC yield and selectivity of ~55% and ~64%, respectively. The reason for La-O catalyst to perform better than other mixed oxide catalysts could be due to its lowest particle size (100 nm) and highest pore volume (15 cm<sup>3</sup> g<sup>-1</sup>) that could have helped reactant molecules (PO and CO<sub>2</sub>) to access the available active catalytic sites with ease. On the other hand, Zr-O catalyst showed the least yield and selectivity of PC. The addition of cerium oxide (Ce<sub>2</sub>O<sub>3</sub>) to Zr-O catalyst gave similar PO conversion (~43%), but exhibited an increase in the yield and selectivity of PC when compared with the experiment conducted using only Zr-O catalyst. Therefore, it could be concluded that the addition of Ce<sub>2</sub>O<sub>3</sub> to Zr-O (i.e. Ce-Zr-O) catalyst was found to be selective in the formation of propylene carbonate as compared to Zr-O catalyst. During the batch experiments, dimers of PO i.e., 2-ethyl-4-methyl-1, 3-dioxolane was detected as a by-product and confirmed by GC analysis. Based on this study, Ce-La-Zr-O catalyst was found to be the

best performed catalyst for synthesis of PC and all further studies were conducted using Ce-La-Zr-O catalyst.



**Figure 5.2.** Effect of different catalysts on the conversion of propylene oxide (PO), selectivity and yield of propylene carbonate (PC). Experimental conditions: Catalyst loading – 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

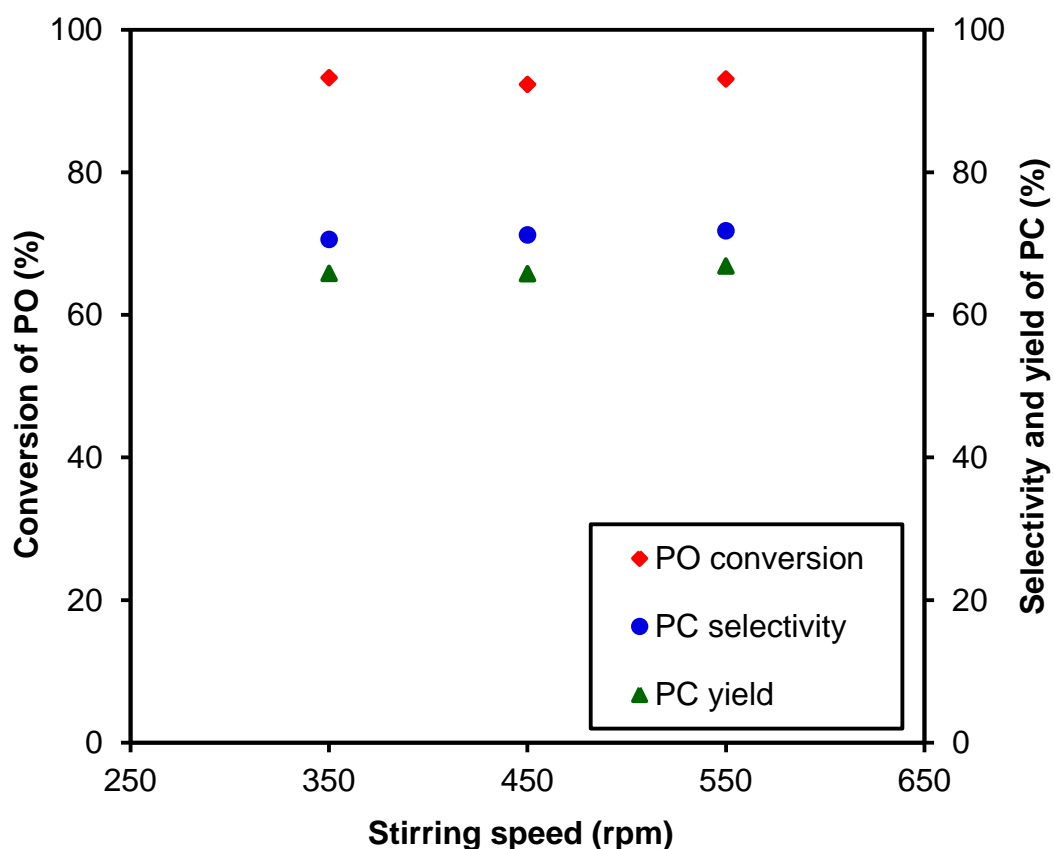
#### 5.3.1.2. Effect of External Mass Transfer Resistance

Important attributes of heterogeneous catalyst include high activity, good stability, ability to recover and reuse, and its selectivity towards a specific product of the reaction. Mass transfer resistance reduces the activity of the catalyst towards the selectivity of the desired product. The activity and selectivity of the solid catalysts thus depends on the catalytic system (i.e., active site, molecular and chemical structures of the catalyst), boundaries

(i.e., internal surface such as pore size and porosity, and external surface such as surface area and particle size) and conditions prevailing at the catalyst boundaries (i.e., temperature and pressure). Heterogeneous catalytic reaction is always connected with mass transfer process. Therefore, understanding the heterogeneous catalytic process could eliminate the effect of mass transfer processes during a chemical reaction.

The effect of external mass transfer resistance on cycloaddition reaction of PO and CO<sub>2</sub> using Ce-La-Zr-O catalyst to produce PC was investigated using a high pressure reactor. The cycloaddition reaction of PO and CO<sub>2</sub> was carried out at different stirring speed of 350–550 rpm. The results are shown in Figure 5.3. It was found that there were no significant changes in the conversion of PO and yield and selectivity of PC when the stirring speed was increased from 350 to 550 rpm considering the experimental error of  $\pm 3\%$ . Since there exists no external mass transfer resistance, it could be concluded that good homogeneous distribution of catalyst particles was possible even at low stirrer speed of 350 rpm (energy efficient process). Therefore, all the subsequent experiments were carried out at a stirring speed of 350 rpm. On the other hand, the catalysts used in this work are fairly uniform, porous and have particle size range of 0.1–30  $\mu\text{m}$  and exhibit pore diameter of 2.7–21.1 nm. Clerici and Kholdeeva (2013) reported that if the pore diameter of the catalyst particles is in the mesoporous region i.e. 2–50 nm, mass transfer limitations could be eliminated. Mass transfer experiments were carried out using different particle size of trimetallic catalyst for alcohol synthesis by Surisetty *et al.* (2010) and they have reported that particles sizes below 254  $\mu\text{m}$  has negligible internal mass transfer resistance. Similarly, absence of both internal and external mass transfer resistances were reported using different stirrer speed and various size fractions of ion-exchange resins as catalysts for synthesis of *n*-Hexyl acetate (Patel and Saha 2007). It was found that a decrease in catalyst particle size permits the entire surface area and pore surface area to participate in the chemical

reaction. For small catalyst particle, reaction is chemically controlled and uninfluenced by mass transfer resistance. In addition, we have investigated the effect of mass transfer at different reaction temperature i.e. 443 K, 458 K and 473 K and found that there was no effect of mass transfer resistances on PC synthesis. Therefore, it can be concluded that there was no effect of mass transfer resistances on the synthesis of PC using Ce-La-Zr-O catalyst.

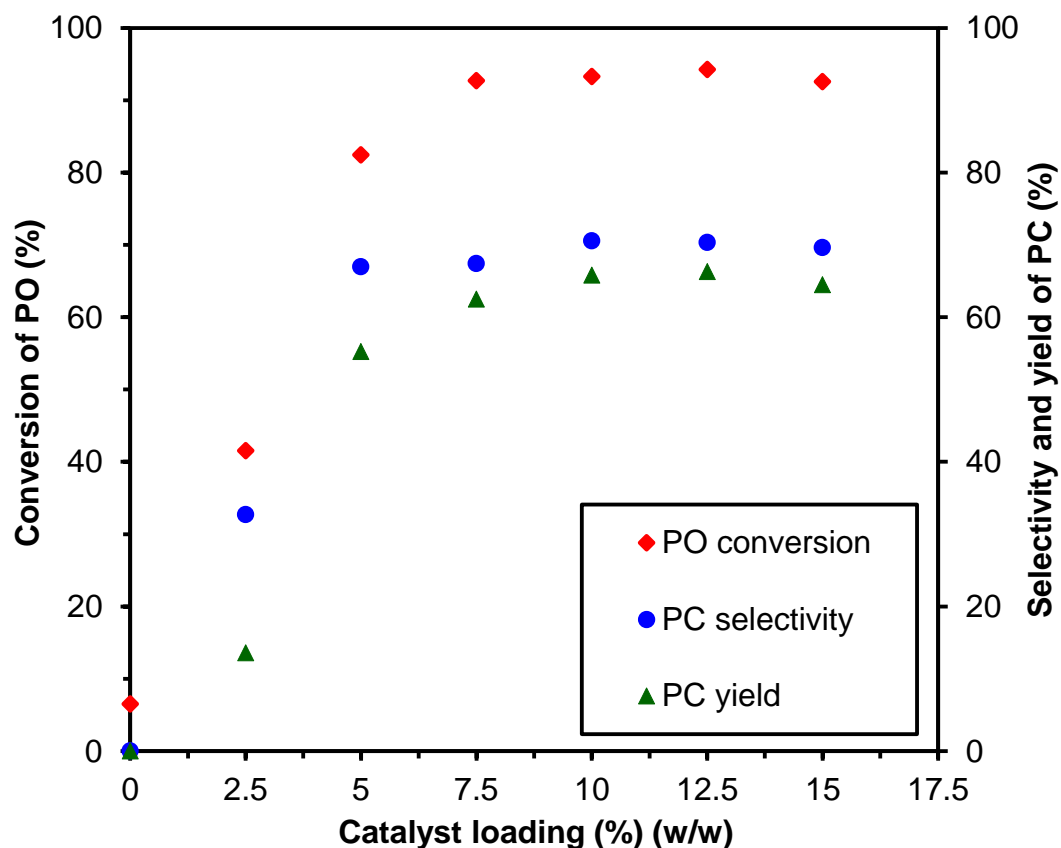


**Figure 5.3.** Effect of external mass transfer resistance on the conversion of propylene oxide (PO) *versus* selectivity and yield of propylene carbonate (PC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h.



### 5.3.1.3. Effect of Catalyst Loading

The catalyst loading for this work is defined as the percentage ratio of mass of catalyst to the mass of limiting reactant (PO). The synthesis of PC was studied with different amounts of Ce-La-Zr-O catalyst at 443 K and 70 bar CO<sub>2</sub> pressure. The results are presented in Figure 5.4. It can be seen from Figure 5.4 that an increase in catalyst loading increases PO conversion, yield and selectivity of PC. For the experiment conducted at 10% (w/w) of catalyst loading, PO conversion, yield and selectivity of PC were ~93%, ~66% and ~72%, respectively. However, for experiment carried out at 15% (w/w) of catalyst loading, PO conversion, yield and selectivity of PC was ~93%, ~65% and 70%, respectively. In view of the experimental error of  $\pm 3\%$ , it seems that the number of active sites for PO and CO<sub>2</sub> to react and produce PC was large enough at 10% (w/w) catalyst loading. Therefore, it was not necessary to increase the catalyst loading above 10% (w/w). Based on this study, catalyst loading of 10% (w/w) was chosen as optimum and all further experiments were conducted at 10% (w/w) catalyst loading.

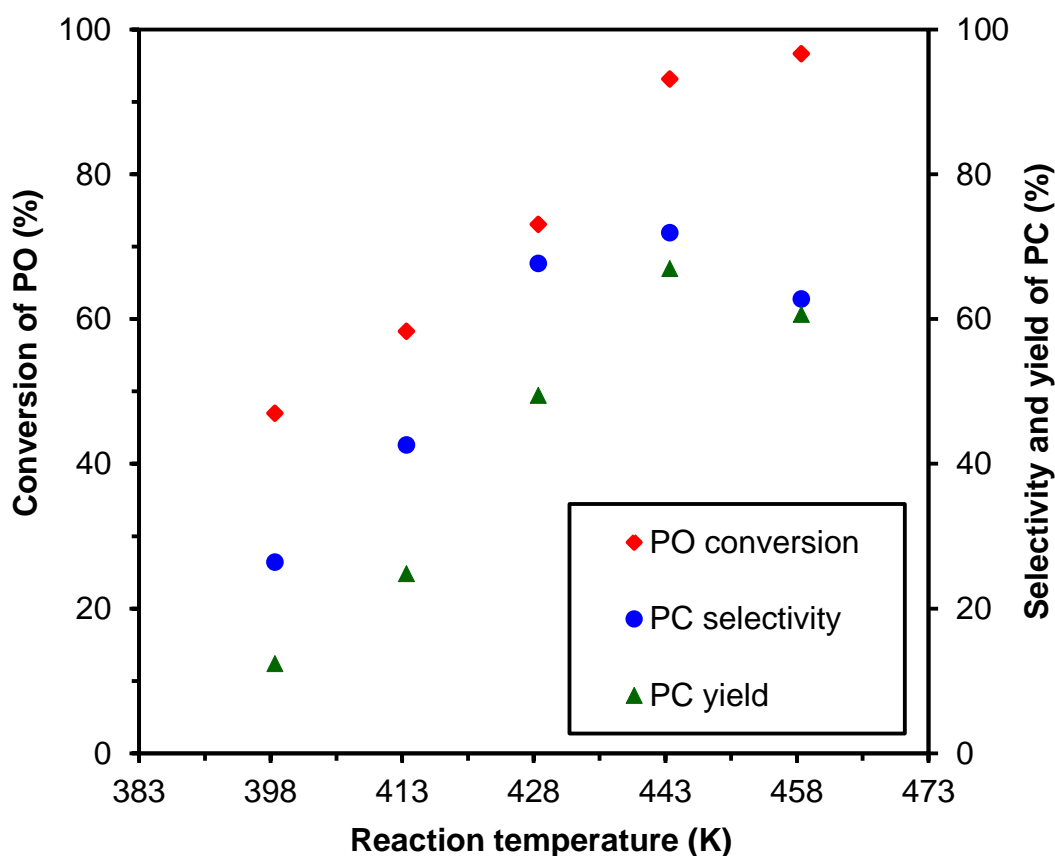


**Figure 5.4.** Catalyst loading dependence on the conversion of propylene oxide (PO) *versus* selectivity and yield of propylene carbonate (PC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

#### 5.3.1.4. Effect of Reaction Temperature

Cycloaddition reaction of PO and CO<sub>2</sub> was carried out at different reaction temperature to study its effect on PO conversion and PC yield and selectivity. Figure 5.5 shows the temperature dependence on the yield and selectivity of PC and on the PO conversion. For this study, all experiments were carried out at 10% catalyst loading and 70 bar CO<sub>2</sub> pressure. The experimental results of this study are plotted in Figure 5.5. It can be observed from Figure 5.5 that an increase in reaction temperature increases PO conversion and PC yield and selectivity. At 443 K, PO conversion and yield and selectivity of PC were 93%, 66% and 72%,

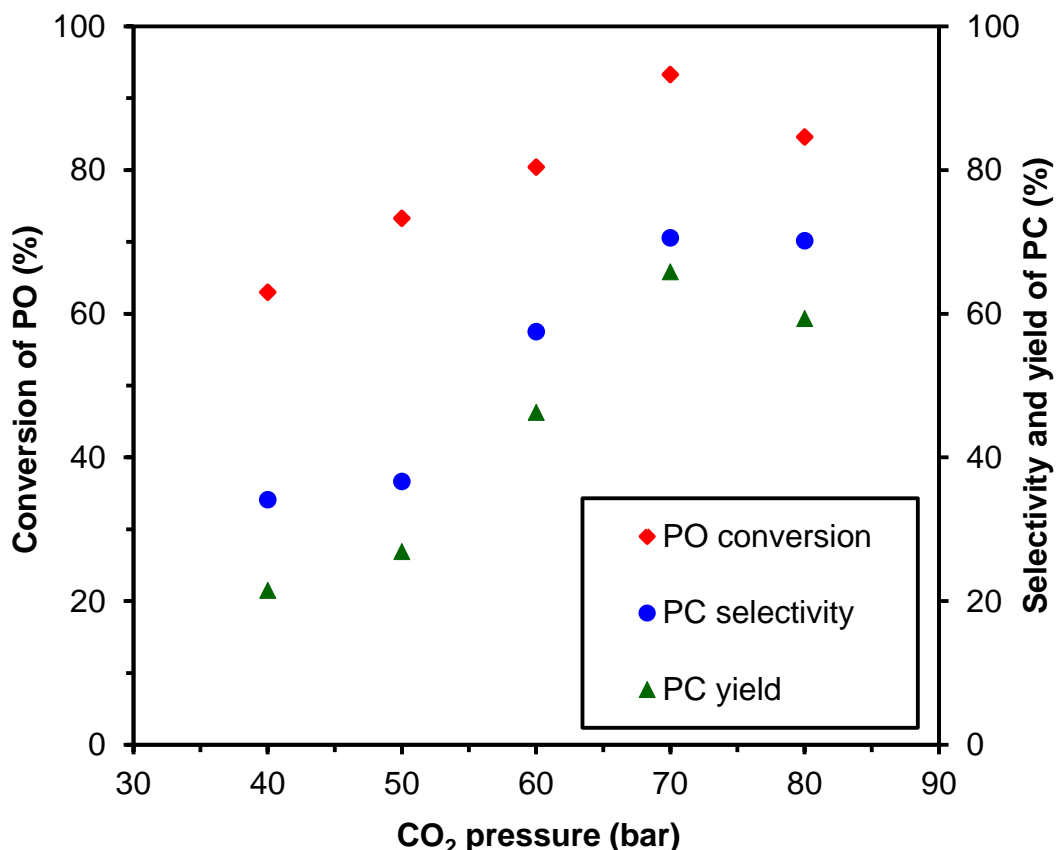
respectively. However, further increase in the reaction temperature from 443 K to 458 K, resulted in the formation of increased amount of 2-ethyl-4-methyl-1, 3-dioxolane. At 458 K, even though the conversion of PO was increased to 97%, the yield and selectivity of PC were decreased to 61% and 63%, respectively when compared to the experiment conducted at 443 K. Yasuda *et al.* (2006) reported that from an industrial point of view, a temperature range of 423–473 K is preferable for cycloaddition reaction of epoxides and CO<sub>2</sub> in the presence of heterogeneous catalysts. All the subsequent experiments for PC synthesis were carried out at 443 K.



**Figure 5.5.** Temperature dependence on the conversion of propylene oxide (PO) versus selectivity and yield of propylene carbonate (PC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

### 5.3.1.5. Effect of Pressure

The reaction of PO and CO<sub>2</sub> to produce PC was investigated at different CO<sub>2</sub> pressure. For this study, the experiments were carried out at 443 K, 10% (w/w) catalyst loading and various supercritical CO<sub>2</sub> (scCO<sub>2</sub>), where scCO<sub>2</sub> acts both as a reagent and as a solvent. Figure 5.6 shows the effect of CO<sub>2</sub> pressure on conversion of PO and on the yield and selectivity of PC formation. It can be observed from Figure 5.6 that an increase in CO<sub>2</sub> pressure increases PO conversion and yield and selectivity of PC. At a CO<sub>2</sub> pressure of 70 bar, the conversion of PO and the yield and selectivity of PC were ~93%, ~66% and ~72%, respectively. However, at a CO<sub>2</sub> pressure of 80 bar, the PO conversion and yield and selectivity of PC decreased to 85%, ~59% and ~70%, respectively. The reasons for such outcomes from this study are inconclusive. However, similar CO<sub>2</sub> pressure effects are often reported for various homogeneous catalyzed systems using supercritical CO<sub>2</sub> (Yasuda *et al.*, 2006). Based on the experimental results, it can be concluded that 70 bar CO<sub>2</sub> pressure was the optimum CO<sub>2</sub> pressure and all the subsequent experiments for the PC synthesis were performed at a CO<sub>2</sub> pressure of 70 bar.

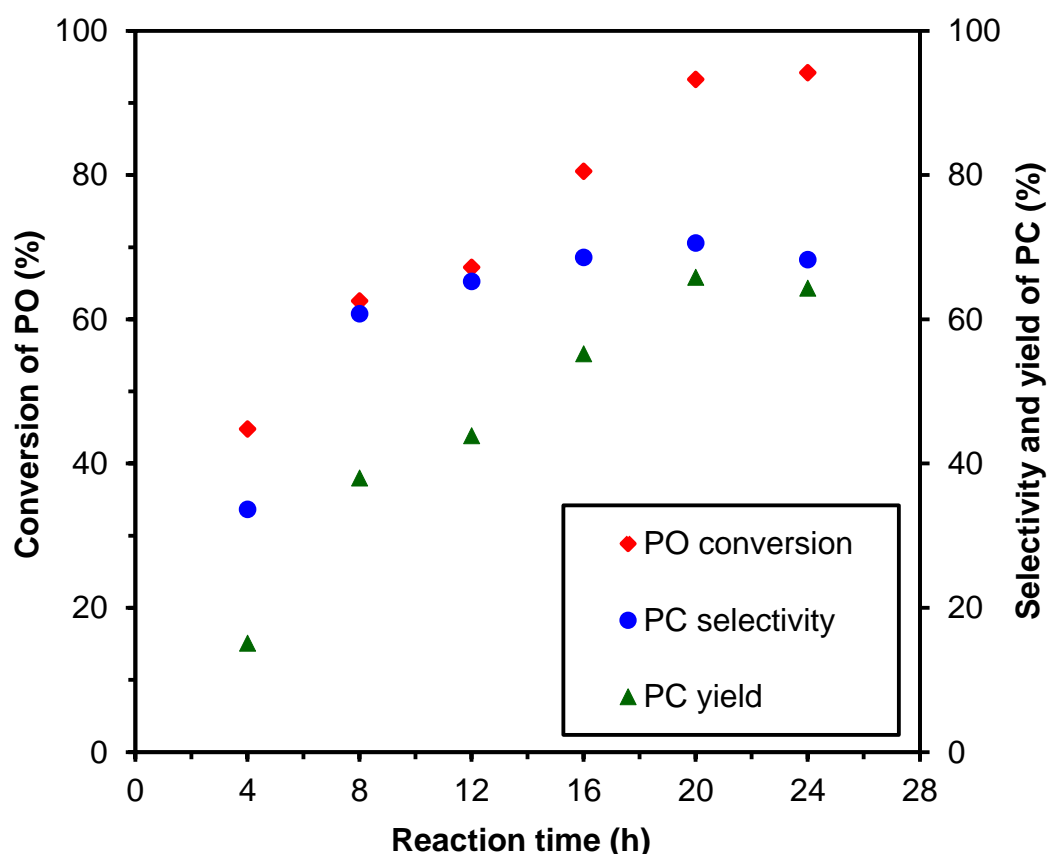


**Figure 5.6.** Pressure dependence on the conversion of propylene oxide (PO) *versus* selectivity and yield of propylene carbonate (PC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; reaction time 20 h; stirring speed 350 rpm.

#### 5.3.1.6. Effect of Reaction Time

A series of experiments were carried out by varying the reaction time to determine the optimum reaction time for synthesis of PC using Ce-La-Zr-O catalyst. All experiments for this study were conducted at 443 K and 70 bar CO<sub>2</sub> pressure. Figure 5.7 illustrates that an increase in reaction time increases PO conversion as well as yield and selectivity of PC. PO conversion of ~63%, ~38% yield and ~61% selectivity of PC was observed for reaction time of 8 h, whereas, ~93% conversion of PO, ~66% yield and ~72% selectivity of PC were obtained for reaction time of 20 h. However, when the reaction was carried out beyond 20 h, i.e., 24 h, the conversion

of PO as well as yield and selectivity of PC were similar to that obtained at 20 h. It can be concluded that the reaction reaches equilibrium at 20 h and the reaction time beyond 20 h would not be beneficial for this reactive system. Based on this study, reaction time of 20 h was considered to be the optimum and all further investigations were carried out at a reaction time of 20 h.

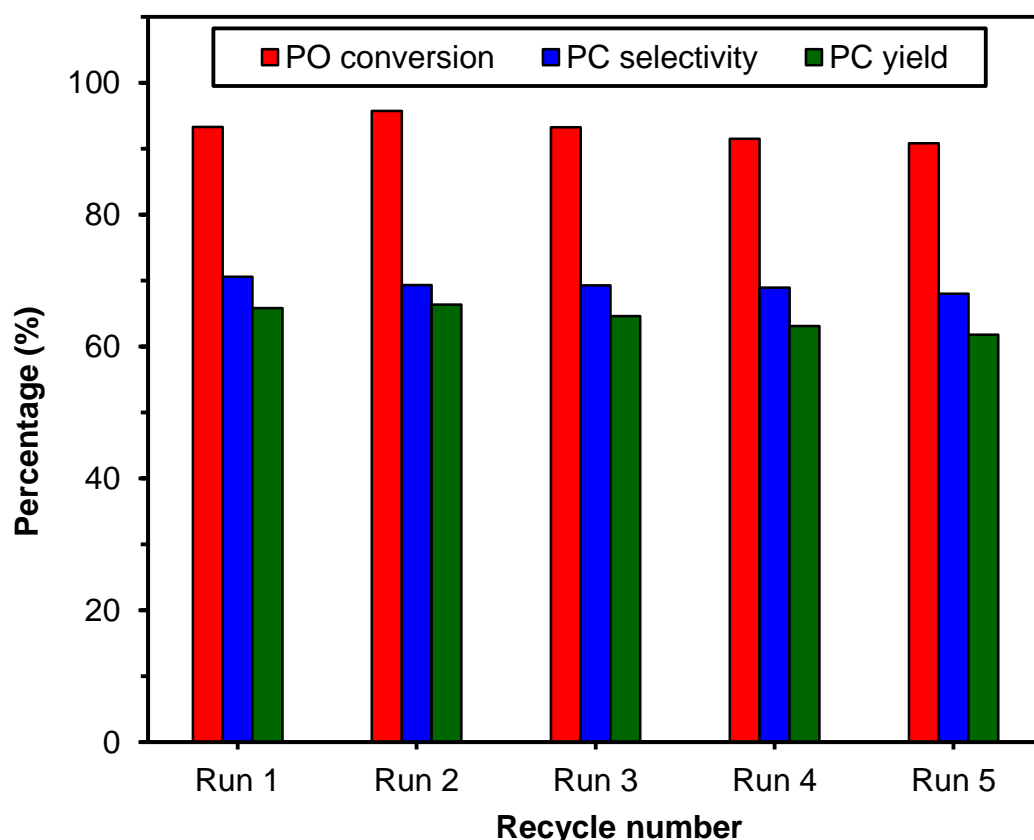


**Figure 5.7.** Time dependence on the conversion of propylene oxide (PO) *versus* selectivity and yield of propylene carbonate (PC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; stirring speed 350 rpm.

#### 5.3.1.7. Catalysts Reusability Studies

The catalyst reusability experiments were carried out to investigate the stability of the best performed heterogeneous catalyst, i.e. Ce-La-Zr-O.

The experiments were carried out in a high pressure reactor using a fresh Ce-La-Zr-O catalyst (10% (w/w) catalyst loading) at a reaction temperature of 443 K, CO<sub>2</sub> pressure of 70 bar and reaction time of 20 h and plotted as Run 1 as shown in Figure 5.8. After Run 1, the catalyst was separated from the reaction mixture by filtration, washed with acetone and recovered by centrifugation. The catalyst was dried in an oven for 12 h at 353 K and reused for Run 2. The same procedure was repeated for subsequent Runs. From Figure 5.8, it is evident that there was no appreciable decrease in the PO conversion and yield and selectivity of PC after several Runs. It can be concluded that ceria and lanthana doped zirconia (Ce-La-Zr-O) catalyst exhibits an excellent reusability and stability for the synthesis of PC and the catalyst can be reused several times without any significant loss in its catalytic activity.



**Figure 5.8.** Catalyst reusability studies on the conversion of propylene oxide (PO), selectivity and yield of propylene carbonate (PC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia

(Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

#### **5.4. Synthesis of Propylene Carbonate using Inorganic Nanocomposite Catalysts Prepared via CHFS Reactor**

Several inorganic nanocomposite catalysts includes ceria, lanthana doped zirconia graphene oxide (Ce<sub>x</sub>-La<sub>y</sub>-Zr<sub>1-(x+y)</sub>O<sub>2</sub>/GO labelled as Ce-La-Zr-GO), ceria, lanthana doped zirconia (Ce<sub>x</sub>-La<sub>y</sub>-Zr<sub>1-(x+y)</sub>O<sub>2</sub> labelled as Ce-La-Zr-O), ceria, doped zirconia graphene oxide (Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/GO labelled as Ce-Zr-GO ) ceria doped zirconia (Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> labelled as Ce-Zr-O), graphene oxide (GO) and zirconia (ZrO<sub>2</sub> labelled as Zr-O) catalysts were prepared using a continuous hydrothermal flow synthesis (CHFS) reactor and investigated for the synthesis of PC from the reaction of CO<sub>2</sub> and PO.

##### **5.4.1. Results and Discussion**

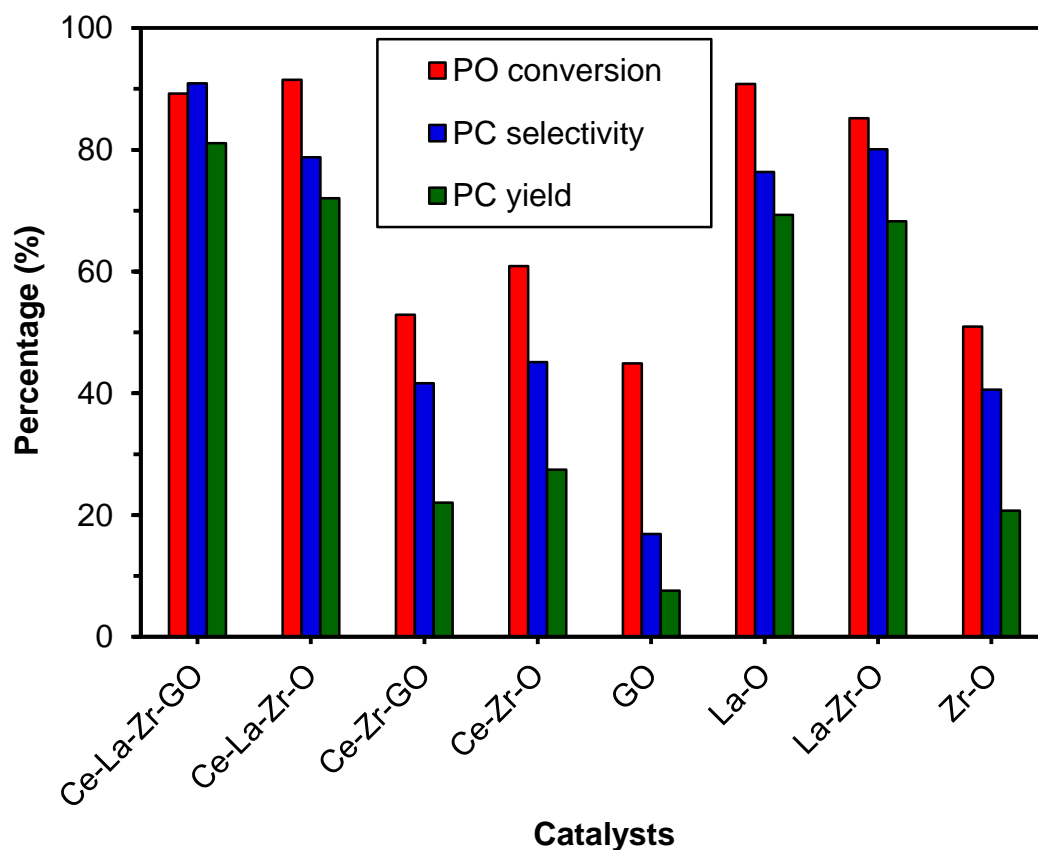
The effect of various parameters such as different catalyst, catalyst heat-treatment temperature, catalyst loading, CO<sub>2</sub> pressure, reaction temperature and time was studied for the optimisation of the reaction conditions. Catalyst reusability studies were also conducted to assess the stability of the catalyst for synthesis of PC using a mechanically stirred Parr high pressure reactor.

##### **5.4.1.1. Effect of Different Catalysts**

For comparative purposes, various heterogeneous catalysts were synthesised using CHFS and investigated for the synthesis of PC from the reaction of CO<sub>2</sub> and PO. Figure 5.9 shows the effect of different catalysts such as ceria, lanthana doped zirconia graphene oxide nanocomposite (Ce<sub>x</sub>-La<sub>y</sub>-Zr<sub>1-(x+y)</sub>O<sub>2</sub>/GO labelled as Ce-La-Zr-GO), ceria, lanthana doped zirconia (Ce<sub>x</sub>-La<sub>y</sub>-Zr<sub>1-(x+y)</sub>O<sub>2</sub> labelled as Ce-La-Zr-O), ceria, doped zirconia graphene oxide (Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/GO labelled as Ce-Zr-GO ) ceria doped zirconia (Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> labelled as Ce-Zr-O), graphene oxide (GO) and zirconia (ZrO<sub>2</sub> labelled as Zr-O) on the conversion of PO, selectivity and



yield of PC. The catalysts were heat-treated at 973 K for 4 h. Ce-La-Zr-O, Ce-Zr-O and Zr-O were heat-treated under air atmosphere while graphene based inorganic nanoparticle (Ce-La-Zr-GO, Ce-Zr-GO and GO) catalysts were heat-treated under nitrogen atmosphere to prevent oxidation of graphene oxide. The reaction of CO<sub>2</sub> and PO to produce PC was carried in a 25 mL mechanical stirrer high pressure reactor at 443 K reaction temperature, 70 bar CO<sub>2</sub> pressure, 10% catalysts loading and 20 h reaction time. It can be seen from Figure 5.9 that Ce-La-Zr-GO catalyst exhibited highest catalytic activity of ~89% conversion of PO, ~90% selectivity and ~81% yield of PC. Ce-Zr-GO catalyst gave ~52% conversion of PO, ~41% selectivity and ~22% yield of PC. However, GO shows least catalytic activity of ~44% conversion of PO, ~16% selectivity and ~7% yield of PC. Ce-La-Zr-O and Ce-La-Zr-GO catalysts prepared using a continuous hydrothermal flow synthesis (CHFS) reactor showed high efficiency as compared to commercially available Ce-La-Zr-O catalyst (MEL Chemicals, UK) when the reaction was carried out at the same reaction condition. The differences in the catalytic performance can be attributed to various parameters including high surface area, particle size, crystallinity and phase composition (Table 3.1). Furthermore, utilising graphene (G) sheet in the formation of inorganic nanocomposite resulted in high catalytic performance of Ce-La-Zr-GO catalysts. In addition, the defects on the G sheet (such as holes, acid or basic groups and presence of residual oxygen, dopant elements, etc.) are recognised as active catalytic sites. Indeed, Ce-La-Zr-O showed lower catalytic activity compared to Ce-La-Zr-O when coupled with GO. Based on this study, it is evident that Ce-La-Zr-GO catalyst shows highest catalytic activity and further studies such as effect of mass transfer resistance, different heat-treatment temperature and catalyst reusability have been investigated in the following sections.

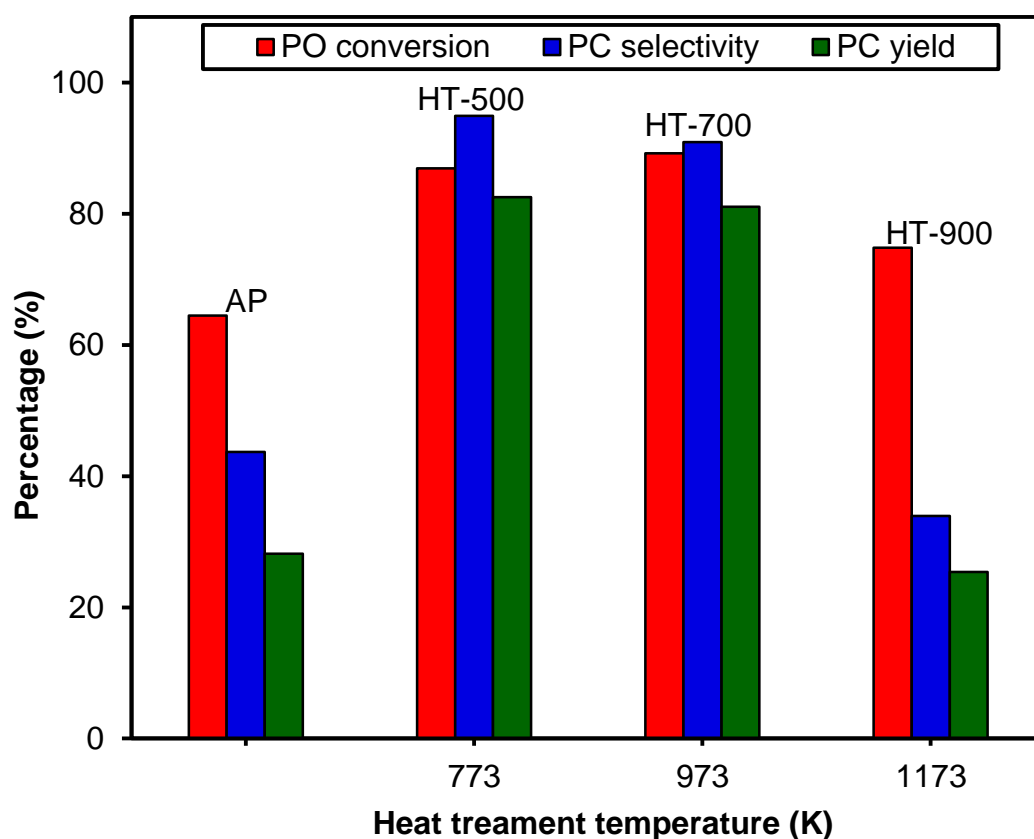


**Figure 5.9.** Effect of different catalysts prepared using a continuous hydrothermal flow synthesis (CHFS) reactor on the conversion of propylene oxide (PO), selectivity and yield of propylene carbonate (PC). Experimental conditions: catalyst heat-treatment – 973 K; catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

#### 5.4.1.2. Effect of Catalyst Heat Treatment Temperature

Few catalytic active materials possess required catalytic properties (activity and selectivity) for the transformation of CO<sub>2</sub> to the desired products. However, they lack the required effective industrial catalytic properties such as mechanical and physicochemical characteristics. An important characteristic of heterogeneous catalysts required for cycloaddition of PO and CO<sub>2</sub> to produce PC include cost effectiveness, easy preparation, reusability, thermal and mechanical stability, resistance to deactivation, poisoning and attrition, and long term stability. Ce-La-Zr-

GO catalyst was prepared using a continuous hydrothermal flow synthesis (CHFS) reactor and heat-treated at different temperature ranging from 773–1173 K to investigate the activity and selectivity for the synthesis of PC. Shown in Chapter 3 (catalyst preparation and characterisation section), Figure 3.5 depicts the photographic image of AP, HT-500, HT-700 and HT-900 catalysts, and Figure 5.10 shows the results of the catalytic performance of Ce-La-Zr-GO catalyst at different heat-treatment temperature. The reaction was carried out in a high pressure reactor, at 10% catalyst loading, 443 K reaction temperature, 70 bar CO<sub>2</sub> pressure and 20 h reaction time. It can be seen in Figure 5.10 that Ce-La-Zr-GO catalyst heat-treated at 773 and 973 K gave very high conversion of PO (~86 and ~89%), selectivity (~94 and ~90%) and yield (~82 and ~81%) of PC, respectively. However, Ce-La-Zr-GO catalyst heat-treated at 1173 K showed the least catalytic activity with ~74% conversion of PO, ~33% selectivity and ~25% yield of PC. Similarly, as prepared Ce-La-Zr-GO (AP) catalyst exhibits the lowest catalytic activity of PO conversion of ~64%, PC selectivity of ~43% and yield of ~28%. The low catalytic activity of HT-900 catalyst was suggested to be due to an increased particle size and consequently lower BET surface area and pore volume (Table 3.1, Chapter 3 catalyst preparation and characterisation section) upon heat-treatment at 1173 K when compared with HT-500 and HT-700 catalysts heat-treated at 773 and 973 K, respectively. Since there was no significant difference in catalytic activity ( $\pm 3\%$ ) of HT-500 and HT-700 catalysts, and considering energy efficient processes, HT-500 catalyst was chosen in the subsequent studies of cycloaddition of PO and CO<sub>2</sub> to produce PC.



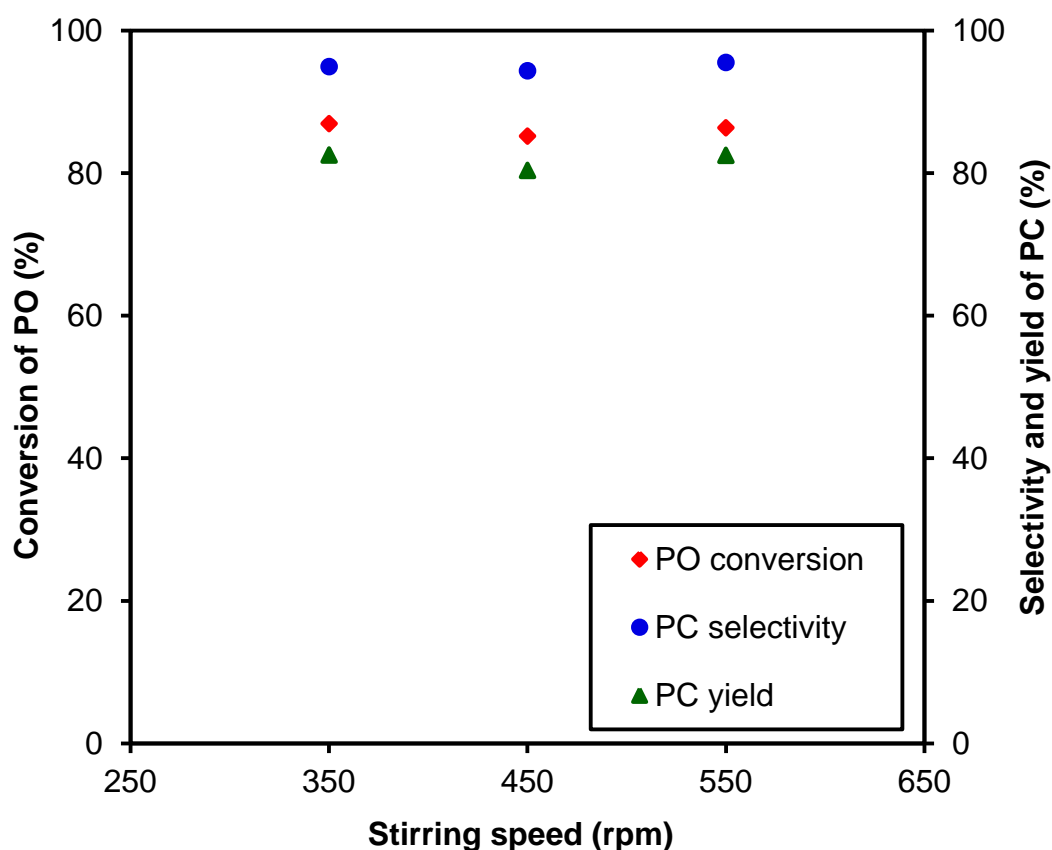
**Figure 5.10.** Catalyst heat-treatment temperature dependence on the conversion of propylene oxide (PO) *versus* (a) yield and (b) selectivity of propylene carbonate (PC). Experimental conditions: catalyst – ceria, lanthana and zirconia graphene (Ce-La-Zr-GO); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

#### 5.4.1.3. Effect of External Mass Transfer Resistance

Catalyst is an important tool in controlling the rate of chemical reaction toward the desired product. The internal and external gradient reduces the catalytic activity and selectivity towards the desired product. In heterogeneous cycloaddition of epoxide and CO<sub>2</sub>, understanding the relationship between the composition, particle size and morphology of the heterogeneous catalysts, effect of mass transfer resistance and the kinetics are important in designing a new catalyst and directing the chemical reaction towards the desired product. During the chemical

reaction, the reaction mixture diffuses through the pores and the film surrounding the solid catalyst. The physicochemical properties (surface area, pore volume and particle size) of the catalyst have an important effect on the activity of the catalyst and consequently the product formation. Deutschmann *et al.* (2009) reported that large nonporous and porous catalyst particles tend to be more affected by mass transfer resistance when compared to powder or fine porous catalyst particles. Since cycloaddition of PO and CO<sub>2</sub> to produce PC is an exothermic reaction, a heterogeneous catalyst with small particles size, porosity, mechanical and thermal stability are important requirements to reduce and eliminate the effect of mass transfer resistance. Therefore, porous powder, graphene inorganic nanocomposite catalysts was synthesised and characterised for the synthesis of PC. The effect of external mass transfer resistance on the cycloaddition reaction of PO and CO<sub>2</sub> to produce PC using HT-500 catalyst was investigated at different stirring speed ranging from 350–550 rpm and the results are presented in Figure 5.11. Effect of external mass transfer resistance was absent as there was no significant change in the conversion (~86%) of PO, selectivity (~94%) and yield (~82%) of PC when the reaction was conducted at different stirring speed (experimental error of  $\pm 3\%$ ). Considering the energy efficiency of the process, 350 rpm was selected for further investigation of cycloaddition reaction of PO and CO<sub>2</sub> to synthesise PC. In addition, the porous powder graphene inorganic nanocomposite catalysts investigated for the synthesis of cyclic carbonate are fairly uniform, with particle size range of 5–26 nm and exhibit an average pore diameter in the region of 2 nm. According to Clerici and Kholdeeva (2013), mass transfer limitation could be eliminated when the pore diameter of the catalyst particles is in the mesoporous region i.e. 2–50 nm. Surisetty *et al.* (2010) analysed the effect of mass transfer using different particle sizes of trimetallic catalyst for alcohol synthesis and found that particles sizes below 254  $\mu\text{m}$  has negligible internal mass transfer resistance. Similarly, Adeleye *et al.* (2014) reported that a decrease in catalyst particle size permits the entire surface area and

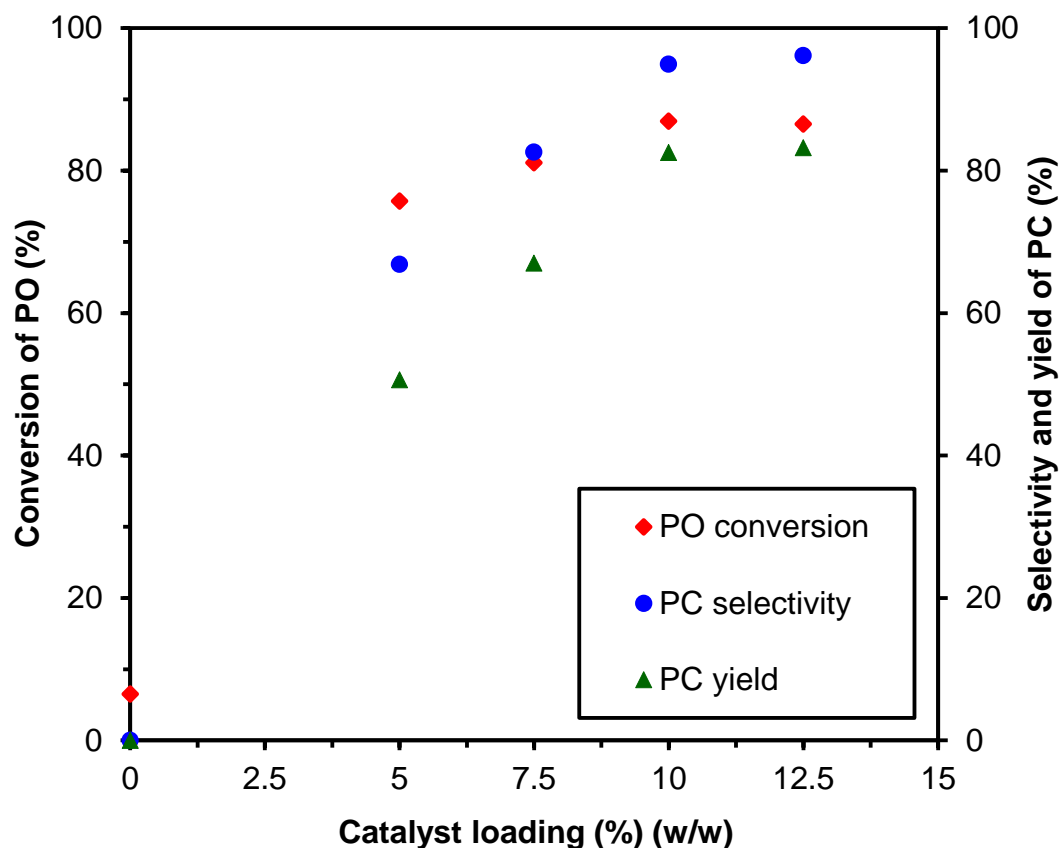
pore surface area to participate in the chemical reaction. For small catalyst particle size (less than 255  $\mu\text{m}$ ), reaction is chemically controlled and uninfluenced by mass transfer resistance. In this case, we speculate that the effect of internal mass transfer resistance could be minimised due to the particle size (2 – 50 nm) and average pore diameter (region of 2 nm) of graphene inorganic nanocomposite catalysts.



**Figure 5.11.** Effect of mass transfer resistance on the conversion of propylene oxide (PO) *versus* selectivity and yield of propylene carbonate (PC). Experimental conditions: catalyst – ceria, lanthana and zirconia graphene (Ce-La-Zr-GO); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h.

### 5.4.1.4. Effect of Catalyst Loading

Catalyst loading for this study can be defined as the ratio of mass of catalyst to mass of reactant. The catalyst loading investigation was carried out to determine the optimum amount of HT-500 catalyst required for the synthesis of PC. Figure 5.12 illustrates the effect of catalyst loading on the conversion of PO, selectivity and yield of PC. When the catalyst loading was increased from 5 to 10% (w/w), steady increase in the conversion of PO (from ~75 to ~86%), selectivity of PC (from ~66 to ~94%) and yield of PC (from ~50 to ~82%) was obtained. However, there was no significant change in the conversion of PO ( $\pm 0.5$ ), selectivity ( $\pm 1$ ) and yield ( $\pm 2$ ) of PC for reaction conducted with 12% catalyst loading. It seems that the number of active catalytic sites for PC synthesis was sufficient at 10% catalyst loading. Hence, there was no need to increase the catalyst loading above 10% (w/w). It can be concluded that 10% catalyst loading is optimum for this study and the same amount of catalyst loading was chosen for further investigations.



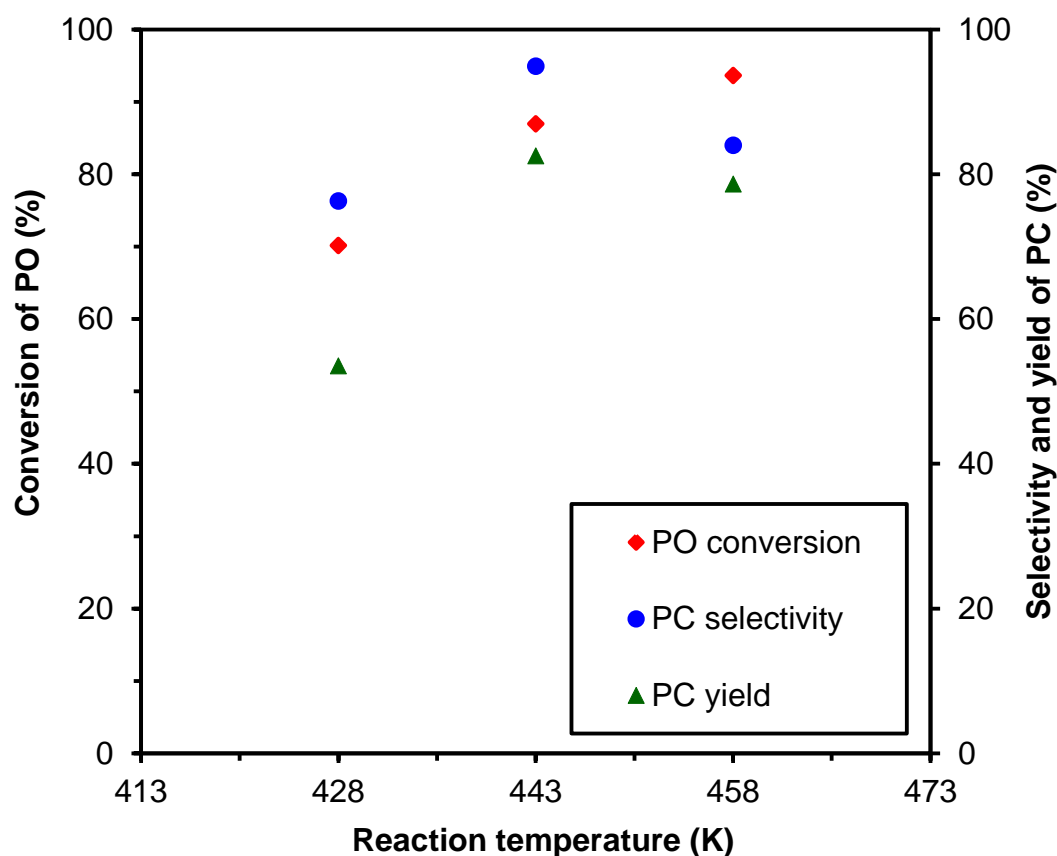
**Figure 5.12.** Catalyst loading dependence on the conversion of propylene oxide (PO) *versus* selectivity and yield of propylene carbonate (PC). Experimental conditions: catalyst – ceria, lanthana and zirconia graphene(Ce-La-Zr-GO); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

#### 5.4.1.5. Effect of Reaction Temperature

The reaction of PO and CO<sub>2</sub> to produce PC was investigated at different reaction temperatures. For this study, the experiments were carried out at 70 bar CO<sub>2</sub> pressure and 10% catalyst loading. Figure 5.13 shows the effect of reaction temperature on the conversion of PC and on the selectivity and yield of PC. It can be observed from Figure 5.13 that with an increase in reaction temperature from 428 K to 443 K, PO conversion, selectivity and yield of PC increase. At a reaction temperature of 443 K, the conversion of PO, selectivity and yield of PC were ~86%, ~94% and ~82%, respectively. At a reaction temperature of 458 K, an increase in the



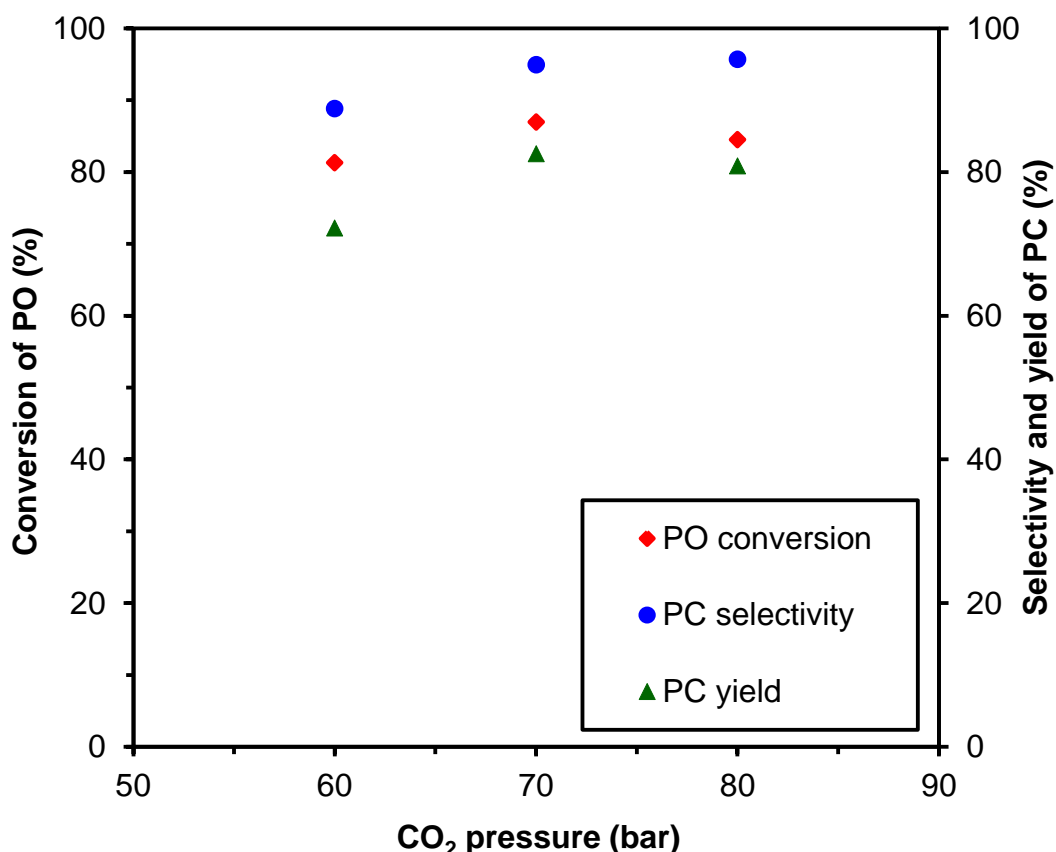
PO conversion (~93%) was achieved, however, decreases in the selectivity and yield of PC to ~84% and ~78%, respectively, was observed. The obtained results are in good agreement with the values reported in the literature where the most effective catalyst performance for PC synthesis (via cycloaddition of PO and CO<sub>2</sub>) are achieved at temperatures ranging from 423–473 K (Srivastava *et al.*, 2006; Yasuda *et al.*, 2006). Based on the experimental results, it can be concluded that 443 K was the optimum reaction temperature and all the subsequent experiments for the PC synthesis were performed at a reaction temperature of 443 K.



**Figure 5.13.** Temperature dependence on the conversion of propylene oxide (PO) versus selectivity and yield of propylene carbonate (PC). Experimental conditions: catalyst – ceria, lanthana and zirconia graphene (Ce-La-Zr-GO); catalyst loading 10% (w/w); reaction time 20 h; CO<sub>2</sub> pressure 70 bar; stirring speed 350 rpm.

### 5.4.1.6. Effect of Pressure

Cycloaddition reaction of PO and CO<sub>2</sub> was carried out at different CO<sub>2</sub> pressure to study its effect on PO conversion and PC selectivity and yield. Figure 5.14 shows the CO<sub>2</sub> pressure dependence on the yield and selectivity of PC and PO conversion. For this study, all experiments were carried out at 10% catalyst loading and 443 K reaction temperature. The experimental results of this study are plotted in Figure 5.14. It can be observed from Figure 5.14 that an increase in CO<sub>2</sub> pressure increases PO conversion and PC selectivity and yield. At 70 bar CO<sub>2</sub> pressure, PO conversion, selectivity and yield of PC were 86%, 94% and 82%, respectively. Further increase in CO<sub>2</sub> pressure to 80 bar gave a decrease in PO conversion (~84%) and PC yield (~80%), but slight increase in PC selectivity (~95%) was observed. The reason for this results are inconclusive and similar CO<sub>2</sub> pressure effects are often observed for several homogeneous catalyzed system using supercritical CO<sub>2</sub> (Yasuda *et al.*, 2006). Pescarmona and Taherimehr (2012) investigated the effect of CO<sub>2</sub> for the synthesis of cyclic carbonate. It was observed that an increase in the CO<sub>2</sub> pressure above the required optimum pressure for cycloaddition reaction of epoxide and CO<sub>2</sub> could lead to the dilution of reaction mixture and reduce the efficiency of cyclic carbonate formation. On the other hand, using CO<sub>2</sub> pressure below the optimum level could lead to an increase in the formation of side products. In this case, the optimum conversion was obtained at a CO<sub>2</sub> pressure of 70 bar and all further experiments were conducted at 70 bar CO<sub>2</sub> pressure.

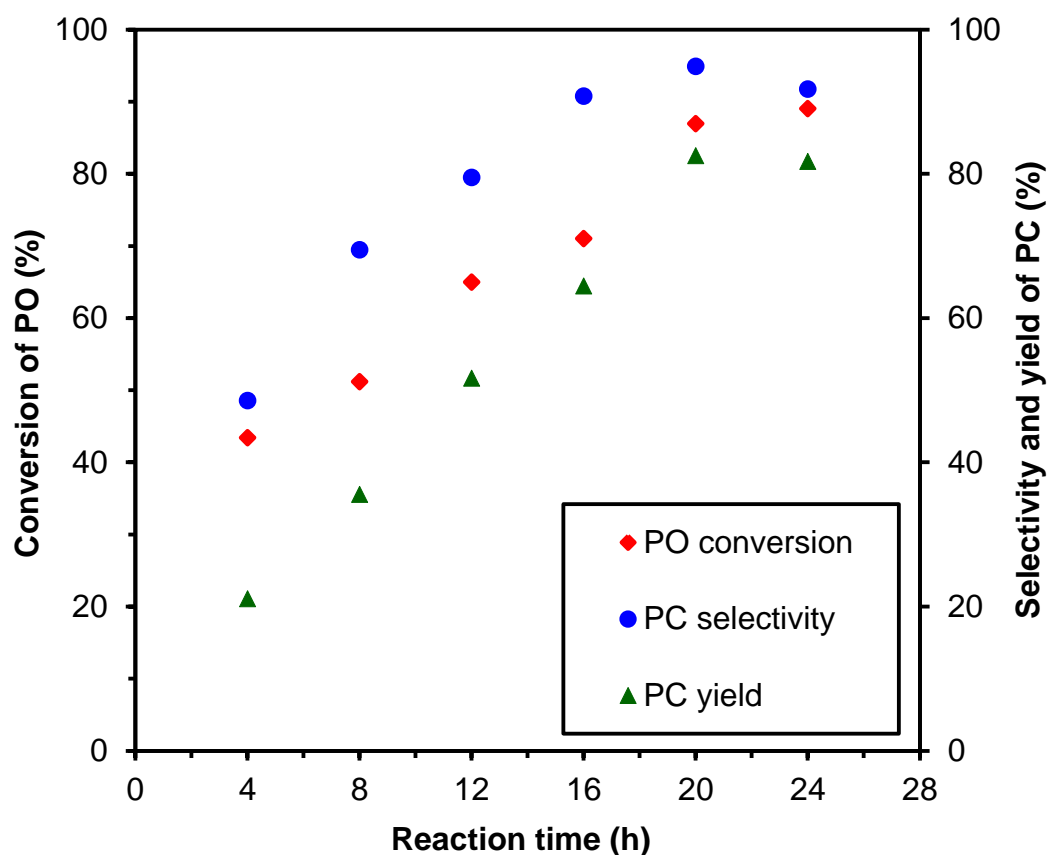


**Figure 5.14.** Pressure dependence on the conversion of propylene oxide (PO) *versus* selectivity and yield of propylene carbonate (PC). Experimental conditions: catalyst – ceria, lanthana and zirconia graphene (Ce-La-Zr-GO); catalyst loading 10% (w/w); reaction time 20 h; reaction temperature 443 K; stirring speed 350 rpm.

#### 5.4.1.7. Effect of Reaction Time

A series of experiments were performed at different reaction time from 4–24 h using HT-500 catalyst at 443 K under CO<sub>2</sub> pressure of 70 bar. The reaction was carried out in a 25 mL high pressure reactor. Figure 5.15 demonstrated the dependence of PO conversion, PC selectivity and yield on reaction time. Steady increase in the conversion of PO, selectivity and yield of PC was observed as the reaction time was increased from 4 h to 20 h. ~86% conversion of PO, ~94% selectivity and 82% yield of PC was achieved at 20 h reaction time, temperature of 443 K and CO<sub>2</sub> pressure of 70 bar. However, higher PO conversion (89%), lower PC selectivity (91%)

and slight decrease in yield (81%) of PC were achieved at 24 h reaction time considering the experimental error of  $\pm 3\%$ . Based on the experimental results, it can be concluded that 20 h reaction time was the optimum reaction time and all the subsequent experiments for the PC synthesis were performed at 20 h reaction time.

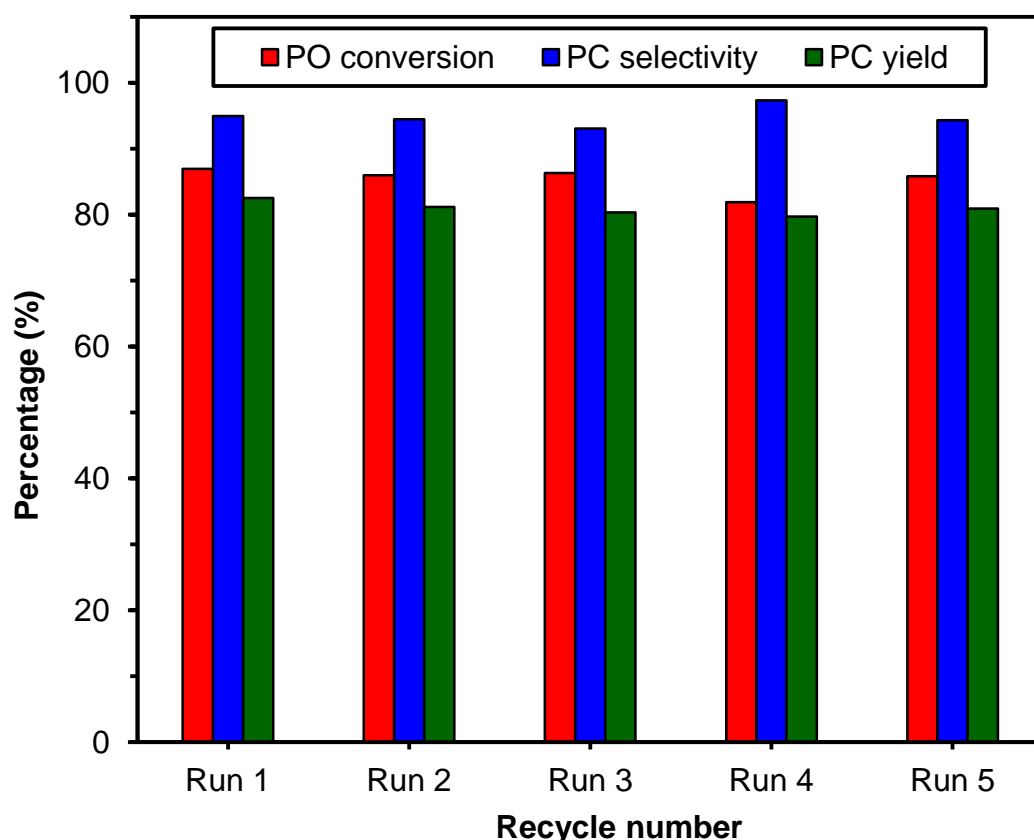


**Figure 5.15.** Time dependence on the conversion of propylene oxide (PO) *versus* selectivity and yield of propylene carbonate (PC). Experimental conditions: catalyst – ceria, lanthana and zirconia graphene (Ce-La-Zr-GO); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; stirring speed 350 rpm.

#### 5.4.1.8. Catalysts Reusability Studies

The important characteristic of effective industrial catalysts is the ability to regenerate without deactivation, resistance to attrition and long lifetime. HT-500 catalyst was prepared and investigated for the stability studies.

The experiments were carried out using a fresh HT-500 catalyst (10% catalyst loading) at a reaction temperature of 443 K, CO<sub>2</sub> pressure of 70 bar and reaction time of 20 h and plotted as Run 1 (shown in Figure 5.16). After Run 1, the catalyst was separated from the reaction mixture by filtration, washed with acetone three times. The catalyst was dried in an oven for 12 h at 353 K and reused for Run 2. The same procedure was repeated for subsequent runs. It is evident from Figure 5.16, there is no significant change in the PO conversion, selectivity and yield of PC after several runs considering the experimental error ( $\pm 3\%$ ). It can be concluded that ceria, lanthana and zirconia graphene oxide (HT-500) catalyst exhibited an excellent reusability and stability for the synthesis of PC and the catalyst can be reused several times without any significant loss in its catalytic activity.



**Figure 5.16.** Catalyst reusability studies on the conversion of propylene oxide (PO), selectivity and yield of propylene carbonate (PC). Experimental conditions: catalyst – ceria, lanthana and zirconia graphene

(Ce-La-Zr-GO); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

### 5.5. Conclusions

The cycloaddition reaction of carbon dioxide (CO<sub>2</sub>) and propylene oxide (PO) for the synthesis of propylene carbonate (PC) was successfully conducted in a high pressure reactor in the presence of various heterogeneous catalysts and without using any organic solvent. It was found that an increase in reaction time increases PO conversion and PC yield and selectivity. Experimental results showed that an increase in reaction temperature above 443 K and CO<sub>2</sub> pressure beyond 70 bar decreases PC yield. Ceria, lanthana and zirconia graphene oxide nanocomposite catalyst synthesised using a continuous hydrothermal flow synthesis (CHFS) reactor and heat-treated at 773 K (HT-500) exhibited highest catalytic activity and its performance was systematically assessed for PC synthesis. The optimum reaction condition was found at 443 K, 70 bar CO<sub>2</sub> pressure, 10% catalyst loading, 20 h reaction time and 350 rpm stirring speed in the presence of HT-500 catalyst. The reusability studies of HT-500 catalyst were conducted to investigate the long term stability of the studied best performed catalyst for PC synthesis. It was found that HT-500 catalyst could be easily separated from the reaction mixture and reused several times without any loss in the catalytic activity for cycloaddition reaction of PO and CO<sub>2</sub>.

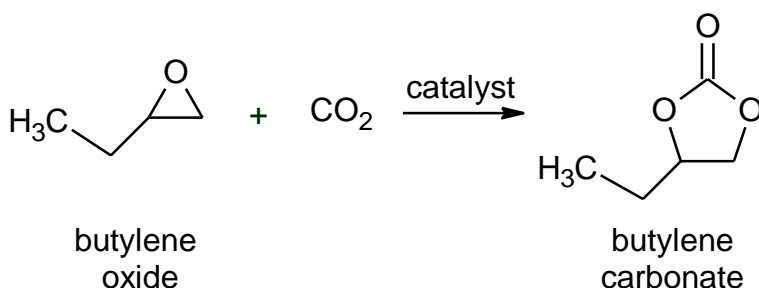
## ***CHAPTER 6***

# ***SYNTHESIS OF BUTYLENE CARBONATE (BC)***

## 6. SYNTHESIS OF BUTYLENE CARBONATE (BC)

### 6.1. Introduction

Butylene carbonate (BC) is an important class of organic carbonate used for a wide range of applications in chemical industry. It is an important reactive intermediate for the preparation of industrially useful compounds such as polymers, surfactant and plasticisers. BC is used as a solvent for separation of catalyst from reaction mixture (catalyst containing phase) in hydroformylation reaction (Behr *et al.*, 2005; Behr *et al.*, 2007; Kumelan *et al.*, 2008). It is also an important solvent used in extraction of phenols, which are toxic pollutants and their removal from industrial waste streams is very crucial from the health and environmental standpoint (Leopold *et al.*, 2005). Synthesis of BC *via* the reaction of BO and CO<sub>2</sub> in the presence of heterogeneous catalysts (Figure 6.1) is discussed in the following section.



**Figure 6.1.** Reaction scheme for butylene carbonate synthesis from cycloaddition reaction of butylene oxide and carbon dioxide.

### 6.2. Experimental Methods

#### 6.2.1. Chemicals

Acetone (99%), *iso*-octane (99.8%), butylene oxide (99.5%), butylene carbonate (98%) were purchased from Fisher Scientific UK Ltd. *n*-Pentane (99.8%) (w/w) was procured from Sigma-Aldrich Co. LLC. The purity of all chemicals was verified by gas chromatography (GC) analysis. These chemicals were used without further purification.



### 6.2.2. Catalysts

Commercially available ceria, lanthana doped zirconia (abbreviated as Ce-La-Zr-O) catalyst was supplied by the Magnesium Elecktron Limited (MEL) and HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K) catalyst was synthesised using a continuous hydrothermal flow synthesis (CHFS) reactor.

### 6.2.3. Experimental Procedure

Cycloaddition reaction of BO and CO<sub>2</sub> was carried out in a 25 mL mechanically stirred Parr high pressure reactor. During any given experiment, the reactor was charged with specific amount of catalyst and the limiting reactant, i.e., BO. The mechanical stirrer was started at a known stirrer speed and the reactor was heated to the desired temperature. Once the desired temperature was achieved, a known amount of liquid CO<sub>2</sub> was fed to the high pressure reactor *via* a supercritical fluid (SCF) pump. The time at which the liquid CO<sub>2</sub> was charged into the reactor was taken as zero time, i.e.,  $t = 0$  and the reaction mixture was left for a desired period. Once the experiment was completed, stirring and heating of the reactor were switched off, the reactor was cooled in an ice bath and the excess CO<sub>2</sub> present in the reactor was vented out. The reaction mixture was filtered and the catalyst was separated, washed with acetone and dried in a vacuum oven.

### 6.2.4. Methods of Analysis

The sample collected from reaction mixture of cycloaddition reaction of butylene oxide (BO) and CO<sub>2</sub> was analysed using a Shimadzu GC-2014 gas chromatography (GC). A ramp method was developed to separate all the components present in the reaction mixture sample. The initial column temperature was maintained at 323 K and the sample was injected by an auto sampler. The column temperature was set to hold at 323 K for 5 min after sample injection. The column temperature was increased to 533 K at the rate of 25°C min<sup>-1</sup>. The total run time for each sample was ~15 min.

*n*-Pentane was used as a solvent to rinse the injection needle after the sample injection. The subsequent sample runs were started when the column temperature was cooled back to 323 K. Internal standard method was used for quantification of all the components present in the sample mixture and *iso*-octane was used as an internal standard. The experimental error for batch studies conducted in a high pressure reactor using the GC technique was in the range of  $\pm 3\%$ .

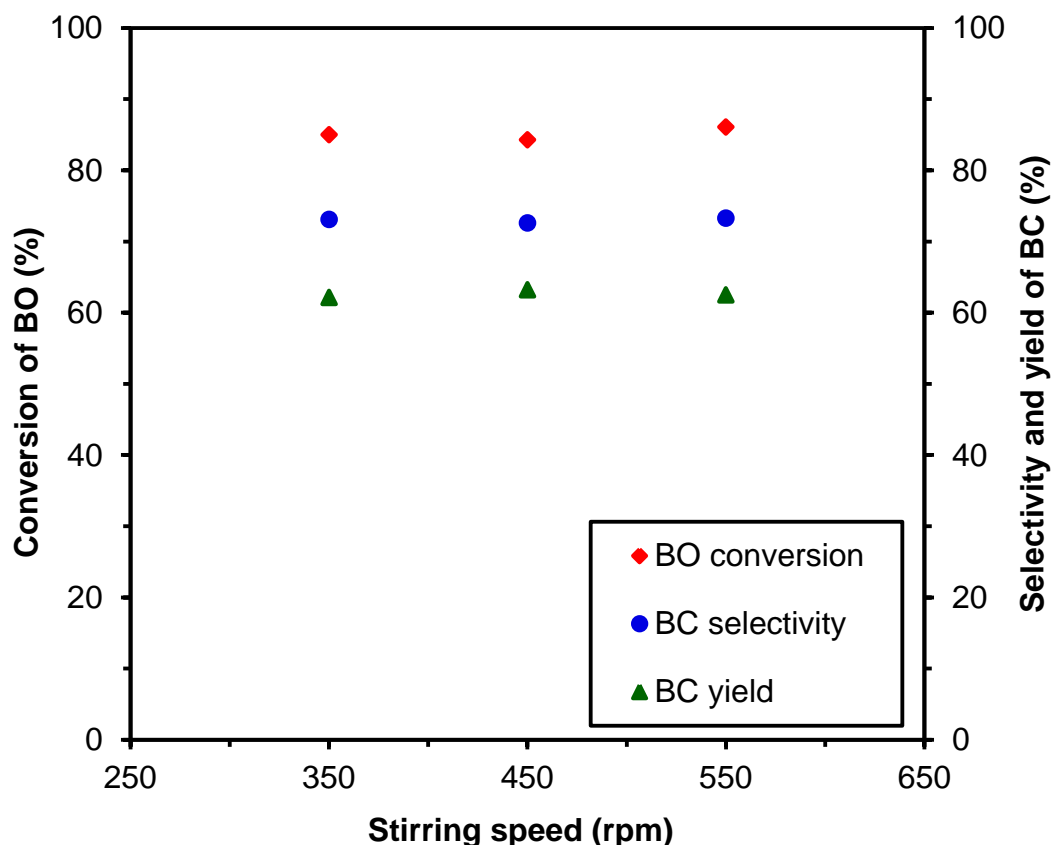
### **6.3. Synthesis of Butylene Carbonate using Commercially Available Ceria, Lanthana Doped Zirconia Catalyst**

#### **6.3.1. Results and Discussion**

The effect of mass transfer resistance, catalyst loading, CO<sub>2</sub> pressure, reaction temperature and reaction time were studied for the optimisation of the reaction conditions for the synthesis of butylene carbonate (BC) using ceria, lanthana doped zirconia (Ce-La-Zr-O) catalyst.

##### **6.3.1.1. Effect of External Mass Transfer Resistance**

The effect of mass transfer resistance on reaction of butylene oxide (BO) and CO<sub>2</sub> using Ce-La-Zr-O catalyst to produce BC was investigated at 443 K reaction temperature and 70 bar CO<sub>2</sub> pressure. The cycloaddition reaction of BO and CO<sub>2</sub> was carried out at different stirring speed of 350–550 rpm in a high pressure batch reactor. The results are presented in Figure 6.2. It was found that there was no significant change in the conversion of BO and yield and selectivity of BC when the stirring speed was increased from 350–550 rpm considering the experimental error of  $\pm 3\%$ . Since there is no external mass transfer resistance, it could be concluded that good homogeneous distribution of catalyst particles was possible even at low stirrer speed of 350 rpm.

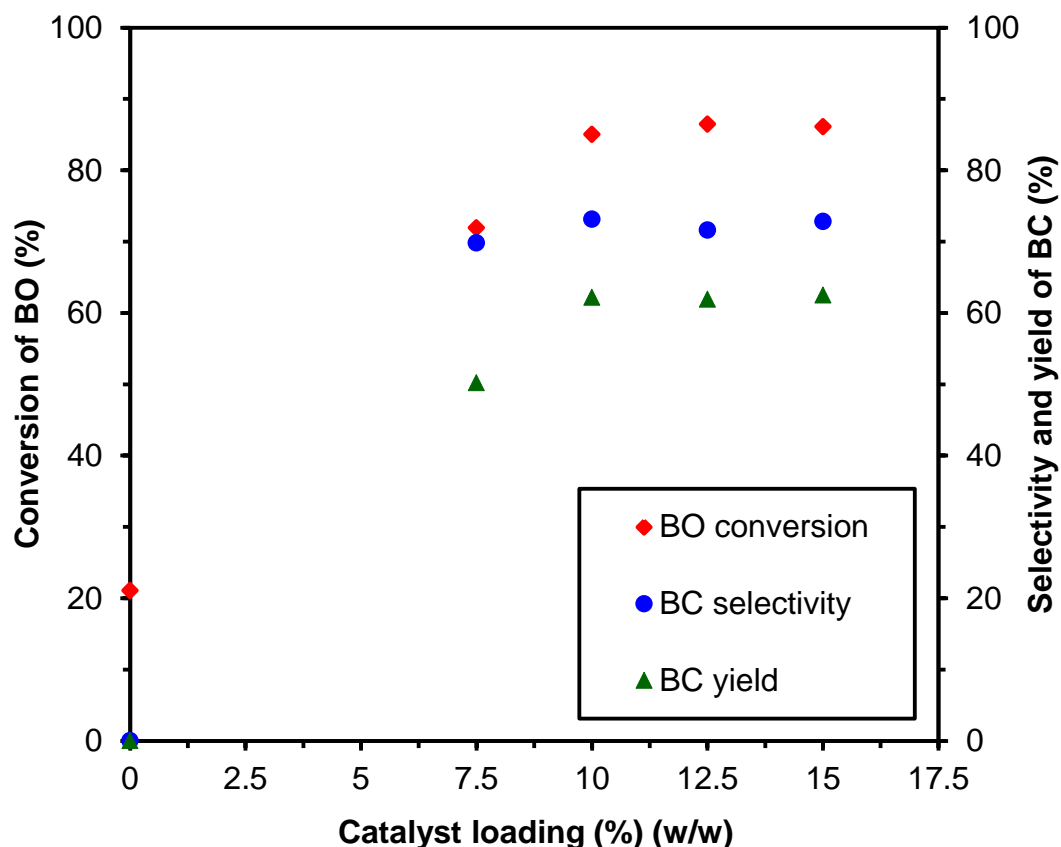


**Figure 6.2.** Effect of external mass transfer resistance on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (PC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h.

#### 6.3.1.2. Effect of Catalyst Loading

In this study, the catalyst loading is defined as the percentage ratio of mass of catalyst to the mass of limiting reactant (BO). The synthesis of BC was studied with different amounts of Ce-La-Zr-O catalyst at 443 K and 70 bar CO<sub>2</sub> pressure. The results are presented in Figure 6.3. It can be seen that an increase in catalyst loading increases BO conversion, yield and selectivity of BC. The control experiment (reaction conducted without catalyst) gave 21% conversion of BO, no selectivity and yield of BC were obtained. For reactions conducted at 7.5% (w/w) catalyst loading, BO conversion, yield and selectivity of BC were ~71%, ~50% and ~69%,

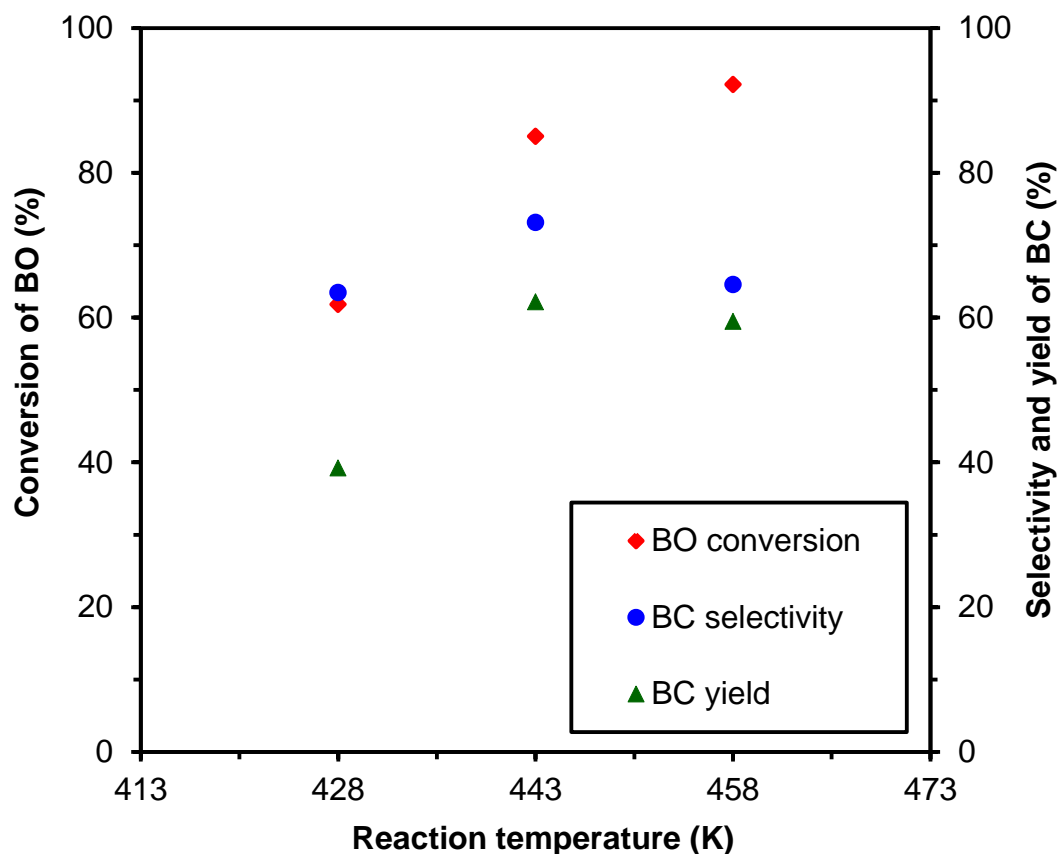
respectively. Further increase in the conversion (~85%) of BO, selectivity (~73%) and yield (~62%) of BC were achieved at 10% (w/w) catalyst loading. When the catalyst loading was increased further to 12.5% and 15% (w/w), there was no significant difference (within  $\pm 2\%$ ) in the conversion BO, selectivity and yield of BC. In view of the experimental error of  $\pm 3\%$ , it seems that the number of active sites for BO and CO<sub>2</sub> to react and produce BC was enough at 10% (w/w) catalyst loading. Therefore, it was not necessary to increase the catalyst loading beyond 10% (w/w). Based on this study, catalyst loading of 10% (w/w) was chosen as an optimum and all further experiments were conducted at 10% (w/w) catalyst loading.



**Figure 6.3.** Catalyst loading dependence on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (BC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

### 6.3.1.3. Effect of Reaction Temperature

The reaction of BO and CO<sub>2</sub> to produce BC essentially requires a thorough screening of reaction temperature in order to achieve adequate BO conversion and BC selectivity. The cycloaddition reactions have been conducted at 428 K, 443 K and 458 K to investigate the effect of reaction temperature on the conversion of BO, selectivity and yield of BC. For this study, the experiments were carried out at 70 bar CO<sub>2</sub> pressure and 10% (w/w) catalyst loading. Figure 6.4 shows the effect of reaction temperature on the conversion of BO and on the selectivity and yield of BC. It can be seen from Figure 6.4 that reaction temperature has a strong effect on the efficiency of BC synthesis. As the reaction temperature was increased from 428 K to 443 K, there was an increase in BO conversion, selectivity and yield of BC. At a reaction temperature of 443 K, the conversion of BO, selectivity and yield of PC were ~85%, ~73% and ~62%, respectively. At a reaction temperature of 458 K, an increase in the BO conversion (~92%) was achieved, however, decrease in the selectivity and yield of BC to ~64% and ~59%, respectively, were observed. The decrease in the selectivity and yield of BC at elevated temperature (458 K) was likely due to the formation of side products such as isomers and dimers of BO. Based on the experimental results, it can be concluded that 443 K was the optimum reaction temperature and all the subsequent experiments for the BC synthesis were performed at a reaction temperature of 443 K.

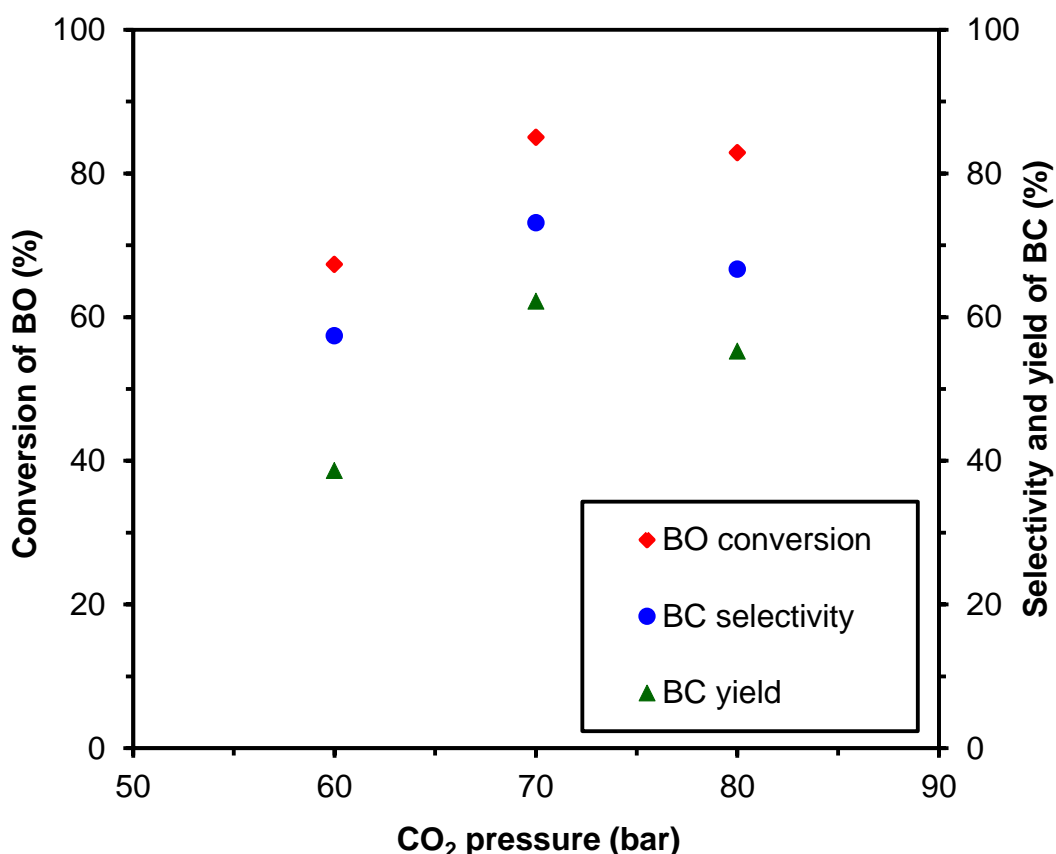


**Figure 6.4.** Temperature dependence on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (BC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

#### 6.3.1.4. Effect of CO<sub>2</sub> Pressure

The effects of varying CO<sub>2</sub> pressure were investigated in order to determine an optimum CO<sub>2</sub> pressure required for the synthesis of BC from addition reaction of BO and CO<sub>2</sub>. Cycloaddition reaction was carried out at 60, 70 and 80 bar to study its effect on BO conversion and BC selectivity and yield. Figure 6.5 showed the CO<sub>2</sub> pressure dependence on BO conversion, selectivity and yield of BC. For this study, all experiments were carried out at 10% (w/w) catalyst loading and 443 K reaction temperature for 20 h. It can be seen from Figure 6.5 that when the CO<sub>2</sub> pressure increased from 60 bar to 70 bar, BO conversion, selectivity and yield of BC

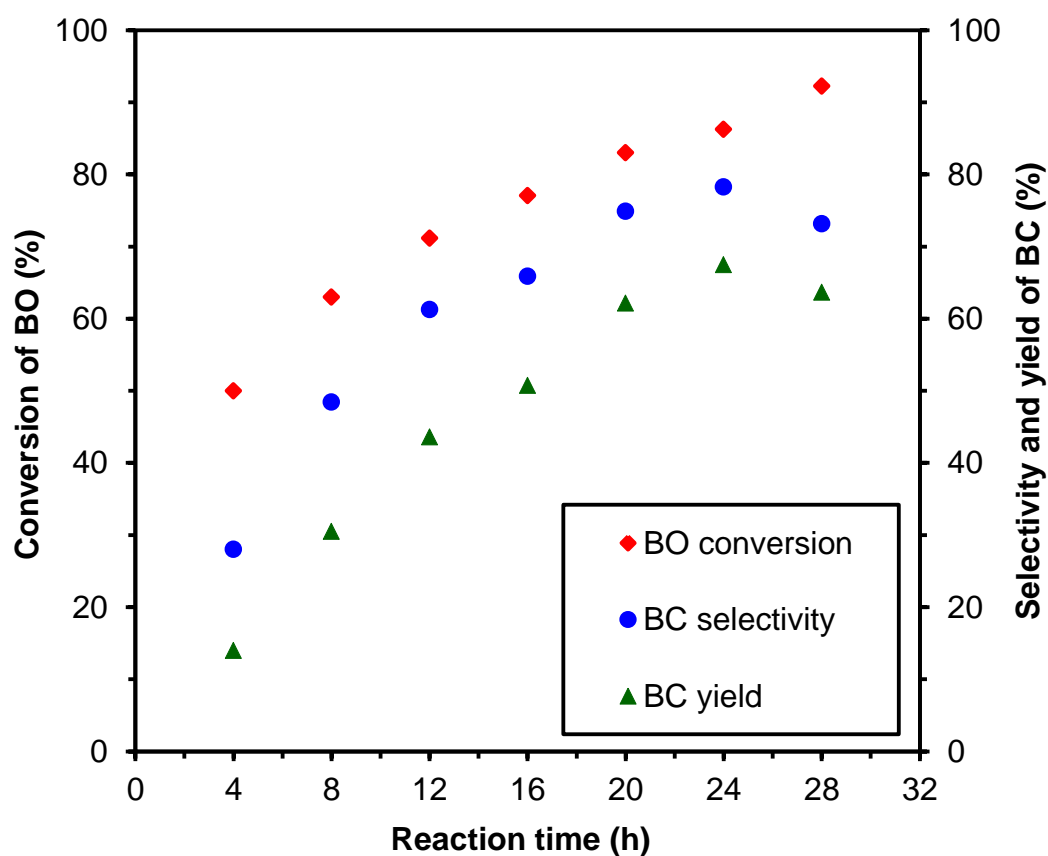
increases from 67% to 85%, 57% to 73% and 38% to 62%, respectively. However, further increase in CO<sub>2</sub> pressure to 80 bar gave a decrease in BO conversion, BC selectivity and yield to 82%, 66% and 55%, respectively. The reason for this results are inconclusive and similar CO<sub>2</sub> pressure effects are often observed in other catalytic system using supercritical CO<sub>2</sub> (Yasuda *et al.*, 2006). The results indicated that an increase in CO<sub>2</sub> pressure above the optimum (70 bar) does not favour the formation of BC which is likely due to dilution effect that retard the interaction of reactants and catalyst (Han *et al.*, 2011). In this case, high efficiency of BC was obtained at a CO<sub>2</sub> pressure of 70 bar, which indicated optimum CO<sub>2</sub> pressure for the reaction of BO and CO<sub>2</sub>.



**Figure 6.5.** Pressure dependence on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (BC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; reaction time 20 h; stirring speed 350 rpm.

### 6.3.1.5. Effect of Reaction Time

Cycloaddition reaction of BC and CO<sub>2</sub> was studied at different reaction time to determine the optimum reaction time for synthesis of BC using Ce-La-Zr-O catalyst. The reactions were conducted at 443 K and 70 bar CO<sub>2</sub> pressure. Figure 6.6 illustrates the effect of reaction time on the synthesis of BC. As the reaction time was increased from 4 h to 24 h, there was an increase in BO conversion as well as selectivity and yield of BC from ~50% to ~86%, ~28% to ~78% and ~14% to ~67%, respectively. When the reaction was carried out beyond 24 h i.e., 28 h, the conversion of BO was further increased to ~92%, however, selectivity and yield of BC were decreased to ~73% and ~63%, respectively. It can be concluded that the reaction attains equilibrium at 24 h and the reaction time beyond 24 h would not be beneficial for this reactive system. Based on this study, reaction time of 24 h was considered to be the optimum.



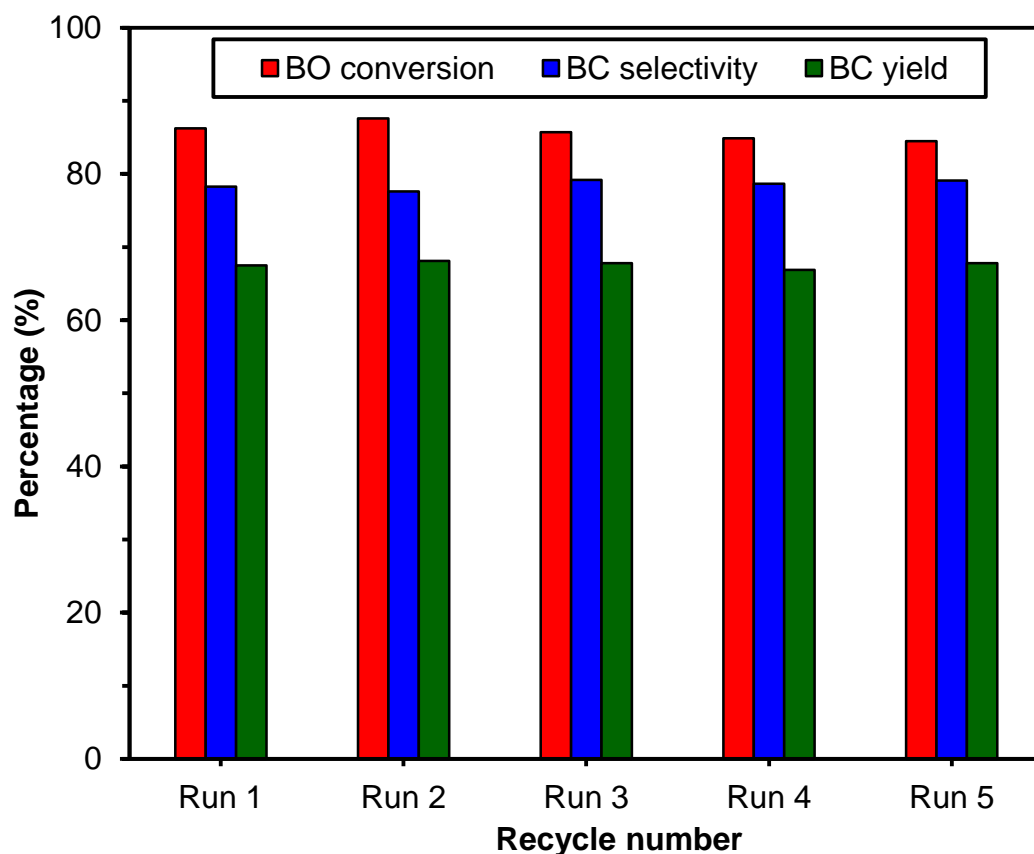
**Figure 6.6.** Time dependence on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (BC). Experimental



conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; stirring speed 350 rpm.

### 6.3.1.6. Catalyst Reusability Studies

Catalyst reusability studies were carried out to investigate the stability of Ce-La-Zr-O catalyst for the synthesis of BC. The experiments were carried out in a high pressure reactor using a fresh Ce-La-Zr-O catalyst (10% (w/w) catalyst loading) at a reaction temperature of 443 K, CO<sub>2</sub> pressure of 70 bar and reaction time of 20 h and plotted as Run 1 as shown in Figure 6.7. After Run 1, the catalyst was separated from the reaction mixture by filtration, washed with acetone and recovered by centrifugation. The catalyst was dried in an oven for 12 h at 353 K and reused for Run 2. The same procedure was repeated for subsequent Runs. From Figure 6.7 it is evident that there was no appreciable decrease in the BO conversion and yield and selectivity of BC after several Runs. It can be concluded that ceria and lanthana doped zirconia (Ce-La-Zr-O) catalyst exhibits an excellent reusability and stability for the synthesis of BC and the catalyst can be reused several times without any significant loss in its catalytic activity.



**Figure 6.7.** Catalyst reusability studies on the conversion of butylene oxide (BO), selectivity and yield of butylene carbonate (BC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 24 h; stirring speed 350 rpm.

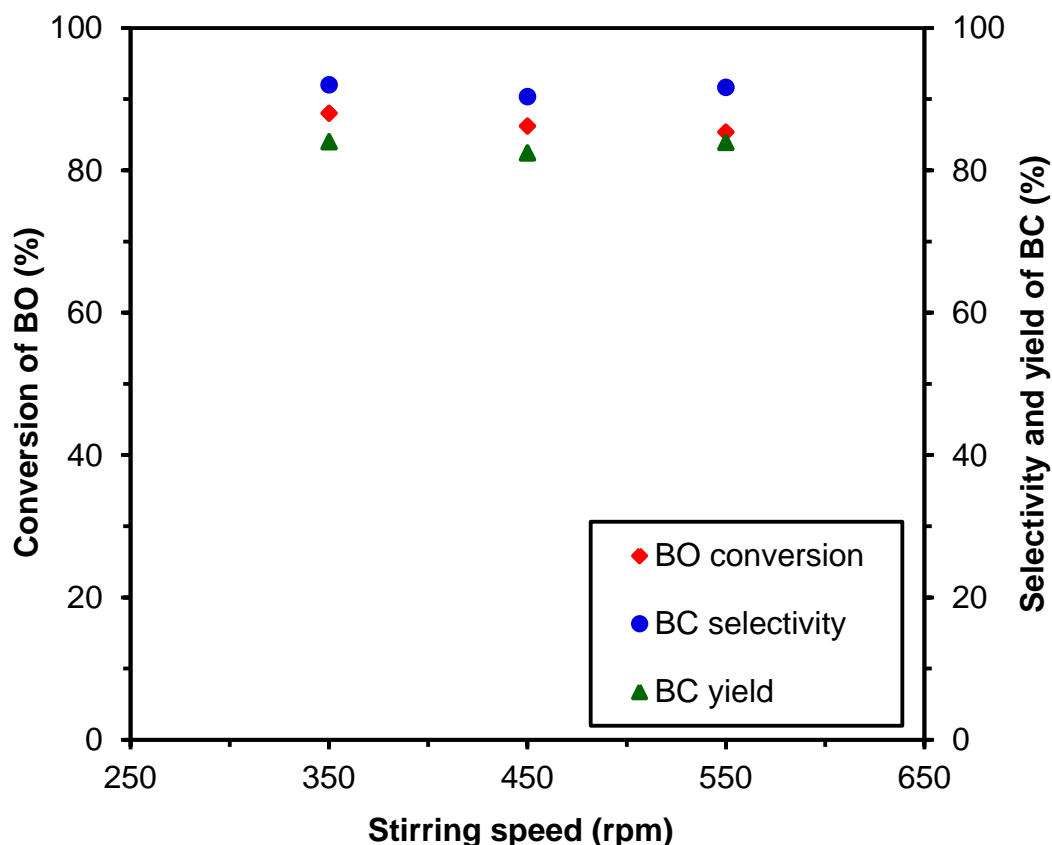
## **6.4. Synthesis of Butylene Carbonate using HT-500 (Ceria, Lanthana and Zirconia Graphene Oxide) Catalyst**

### **6.4.1. Results and Discussion**

The effect of mass transfer resistance, catalyst loading, CO<sub>2</sub> pressure, reaction temperature and time were studied for the optimisation of the reaction conditions for the synthesis of butylene carbonate (BC) using HT-500 (ceria, lanthana and zirconia graphene) catalyst. Catalyst reusability studies have been conducted to investigate reusability and stability of the catalyst for the synthesis of BC.

#### **6.4.1.1. Effect of External Mass Transfer Resistance**

Mass transfer limitations can be a major factor that affects the efficiency of organic carbonate synthesis in heterogeneously catalysed process. In heterogeneous cycloaddition reaction of butylene oxide (BO) and CO<sub>2</sub> using batch high pressure reactor, the effect of external mass transfer resistance on the catalytic activity of HT-500 catalyst was investigated at different stirring speed ranging from 350–550 rpm, and reaction conditions of 443 K temperature, 70 bar CO<sub>2</sub> pressure and 10% (w/w) catalyst loading. The results are presented in Figure 6.8. It was observed that varying stirring speed had no significant effect on the catalytic performance of HT-500 catalyst. As such, no significant change in the conversion of BO, selectivity and yield of BC when the reaction was conducted at different stirring speed (experimental error of  $\pm 3\%$ ). Considering the energy efficiency of the process, 350 rpm was selected for further investigation of cycloaddition reaction of BO and CO<sub>2</sub> to synthesise BC. Similar external mass transfer effect was observed in the synthesis of PC from cycloaddition reaction of PO and CO<sub>2</sub> using HT-500 catalyst (Adeleye *et al.*, 2015).

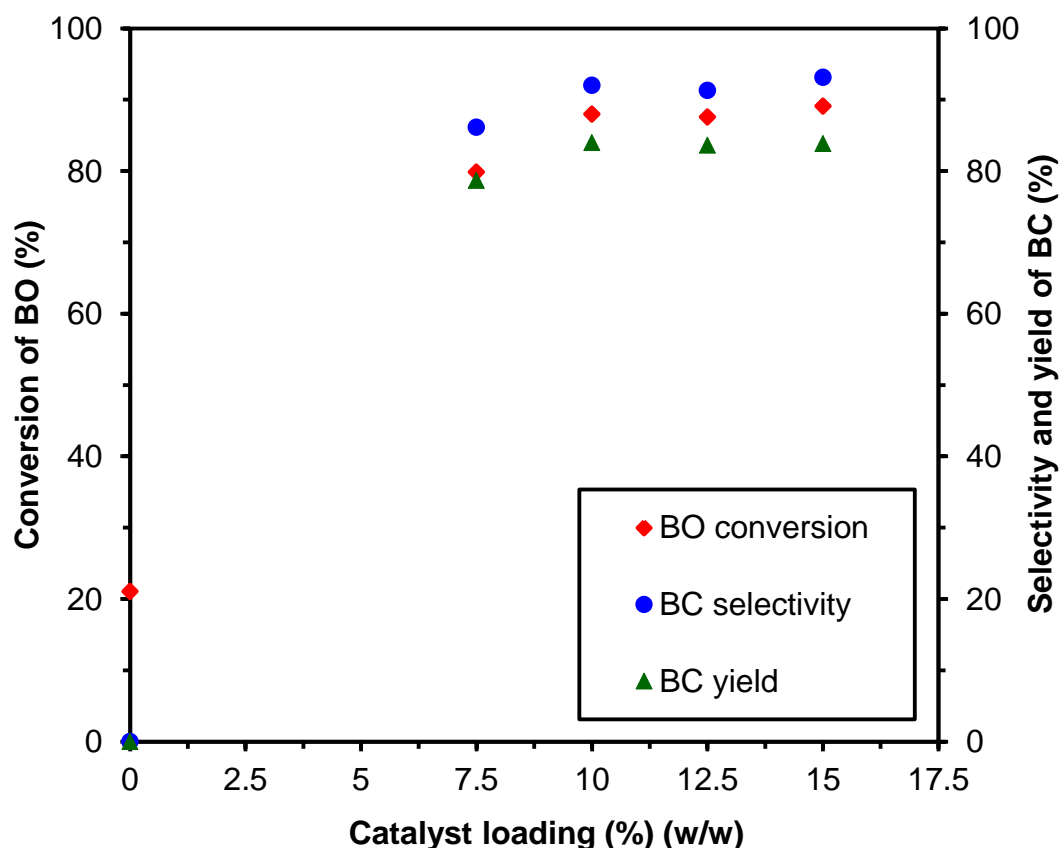


**Figure 6.8.** Effect of external mass transfer resistance on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (PC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 24 h.

#### 6.4.1.2. Effect of Catalyst Loading

The influence of varying the catalyst loading on the synthesis of BC was studied by carrying out a set of addition reactions of BO and CO<sub>2</sub> using different amount of HT-500. The results are presented in Figure 6.9. BO conversion of ~79%, BC selectivity of ~86% and yield of ~78% were achieved when the reaction was carried out using 7.5% (w/w) catalyst loading. This linearly increased to BO conversion of ~88%, BC selectivity of 92% and yield of ~84% when catalyst loading increased to 10%. Similar BO conversion, BC selectivity and yield were achieved when catalyst

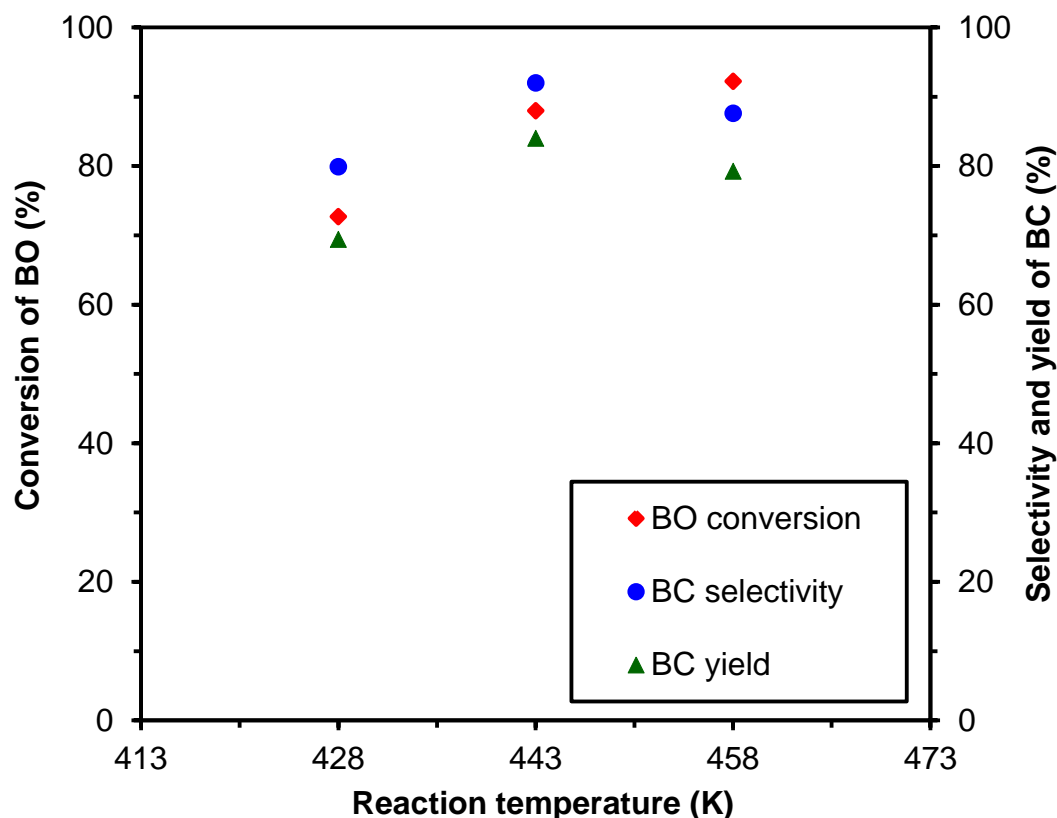
loading increased to 12.5% (w/w) and therefore it was not necessary to increase the catalyst loading above 10% (w/w). In view of the experimental error of  $\pm 3\%$ , it seems that the number of active sites required for BO and CO<sub>2</sub> to react and produce BC was sufficient at 10% (w/w) catalyst loading. The results show that 10% (w/w) catalyst loading is the optimum amount of catalyst required for this reaction.



**Figure 6.9.** Catalyst loading dependence on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (BC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 24 h; stirring speed 350 rpm.

### 6.4.1.3. Effect of Reaction Temperature

The effect of reaction temperature on the BO conversion, BC selectivity and yield was studied in order to optimise the reaction conditions. A set of catalytic reactions was conducted at 70 bar within a temperature range of 428 and 458 K for 24 h. Figure 6.10 shows the temperature dependence of BC synthesis using HT-500 as a catalyst. It is obvious that reaction temperature has a significant effect on the synthesis of BC. BO conversion and BC selectivity and yield increased with an increase in temperature from 428 K to 443 K. Further increasing the temperature beyond 443 K gave an increase in the BO conversion, decrease in the selectivity and yield of BC. The decrease in the efficiency (selectivity and yield) of BC synthesis at elevated temperature (458 K) was likely due to an increase in the formation of side products, which include isomers and dimers of BO. Therefore, this study indicates that 443 K is the optimum temperature for the reaction between BO and CO<sub>2</sub>. Similar reaction temperature effect on the heterogeneous catalysed processes for organic carbonates syntheses have been reported in the literature (Srivastava *et al.*, 2006; Yasuda *et al.*, 2006; Adeleye *et al.*, 2015).

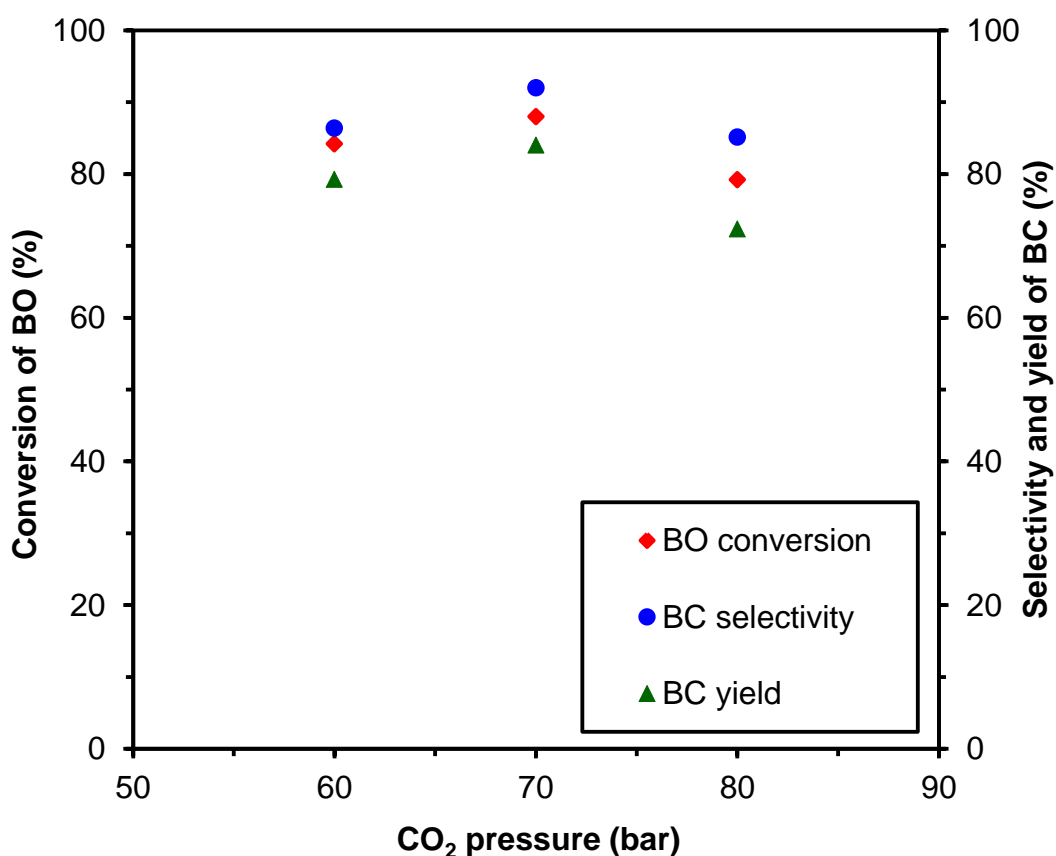


**Figure 6.10.** Temperature dependence on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (BC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); CO<sub>2</sub> pressure 70 bar; reaction time 24 h; stirring speed 350 rpm.

#### 6.4.1.4. Effect of CO<sub>2</sub> Pressure

Several published literature have shown that CO<sub>2</sub> pressure at its supercritical state or near supercritical state (73.3 bar) is important for improved mass transfer of the reactants in heterogeneous catalysed processes, which includes synthesis of organic carbonate from cycloaddition reaction of epoxide and CO<sub>2</sub> ( Du *et al.*, 2005; Yasuda *et al.*, 2006; Adeleye *et al.*, 2014 and 2015). The effect of CO<sub>2</sub> pressure on the BO conversion, selectivity and yield of BC was studied in order to assess the optimum CO<sub>2</sub> pressure for the synthesis of BC using HT-500 as a catalyst. The experiments were conducted in a high pressure batch reactor at 443 K within a pressure range of 60 – 90 bar for 24 h and the

results are shown in Figure 6.11. It can be seen from Figure 6.11 that an increase in CO<sub>2</sub> pressure increases BO conversion, selectivity and yield of BC. At a CO<sub>2</sub> pressure of 60 bar, BO conversion and selectivity and yield of BC were ~84%, ~86% and ~79%, respectively. As the CO<sub>2</sub> pressure was further increased to 70 bar, BO conversion, selectivity and yield of BC increased to ~88%, ~92% and ~84%, respectively. However, further increase in CO<sub>2</sub> pressure to 80 bar showed decrease in the BO conversion or selectivity and yield of BC, which is likely due to the dilution effect at elevated CO<sub>2</sub> pressure. Therefore, from this study, it can be concluded that the optimum CO<sub>2</sub> reaction pressure is 70 bar.

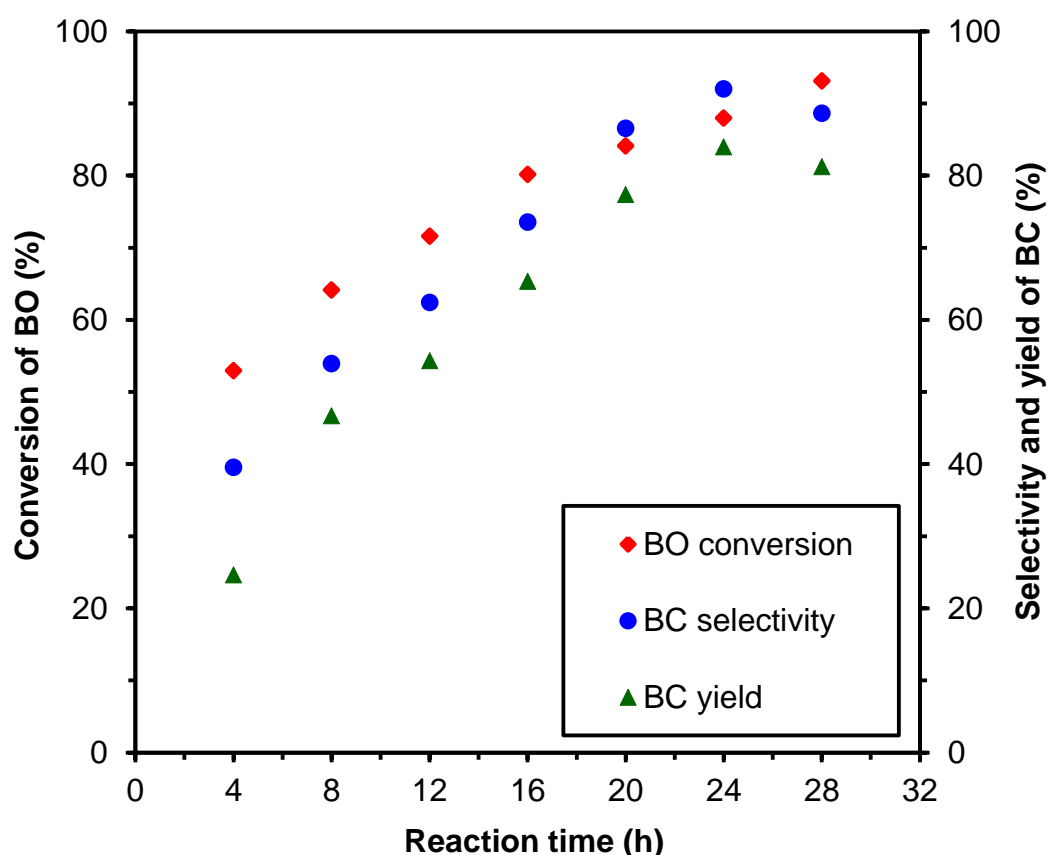


**Figure 6.11.** Pressure dependence on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (BC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); reaction temperature 443 K; reaction time 24 h; stirring speed 350 rpm.



#### 6.4.1.5. Effect of Reaction Time

The influence of varying the reaction time on the efficiency of synthesis of BC was studied by carrying out a set of cycloaddition reactions of BO to CO<sub>2</sub> in the presence of the HT-500 catalyst and the results are shown in Figure 6.12. A BO conversion of ~53%, BC selectivity of ~39 and yield of ~24% were achieved when the reaction was carried out for 4 h, which was steadily increased to ~88%, ~92 and ~84%, respectively, when the reaction time was steadily increased to 24 h. These results clearly show that at prolonged reaction time beyond 24 h and up to 28h, further increase in the BO conversion to ~93, decrease in the BC selectivity to ~88% and yield to ~81% were obtained, indicating that 24 h is the optimum reaction time for the catalysed reaction of BO and CO<sub>2</sub> to produce BC.

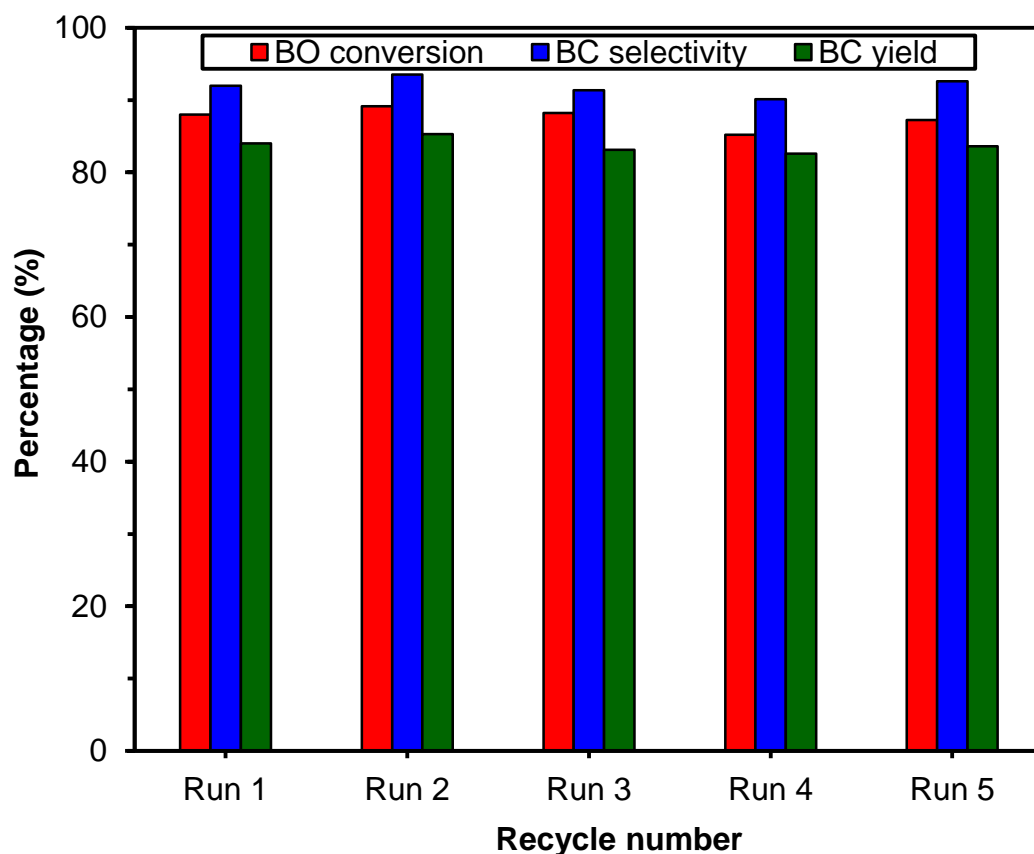


**Figure 6.12.** Time dependence on the conversion of butylene oxide (BO) *versus* selectivity and yield of butylene carbonate (BC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia

graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; stirring speed 350 rpm.

### 6.4.1.6. Catalysts Reusability Studies

Catalyst reusability of HT-500 catalyst was studied by carrying out a set of reactions at the optimum reaction conditions obtained from the batch studies, i.e., at 443 K reaction temperature, 70 MPa CO<sub>2</sub> pressure, 24 h reaction time and 10% (w/w) catalyst loading. The HT-500 catalyst recovered from the batch study at optimised reaction condition (Run 1) was washed three times with acetone, dried in an oven for 12 h at 353 K and reused (Run 2). The same procedure was repeated for subsequent reactions at the same reaction conditions (Run 3 – 5). The results are presented in Figure 6.13. It is interesting to note that there was no significant change in results (BO conversion, BC selectivity and yield) as compared to the fresh catalyst (Run 1), indicating that HT-500 can be reused more than 5 times without any significant loss its catalytic activity.



**Figure 6.13.** Catalyst reusability studies on the conversion of butylene oxide (BO), selectivity and yield of butylene carbonate (PC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 24 h; stirring speed 350 rpm.

### 6.5. Conclusions

Commercially available Ce-La-Zr-O catalyst and HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K) catalyst prepared using continuous hydrothermal flow synthesis (CHFS) reactor were successfully assessed for their catalytic activity for the synthesis of butylene carbonate (BC) from the cycloaddition of butylene oxide (BO) and CO<sub>2</sub> without using any organic solvent. HT-500 catalyst exhibited highest catalytic activity as compared to other heterogeneous catalysed processes. The optimum reaction condition was found at 443 K,

70 bar CO<sub>2</sub> pressure, 10% catalyst loading, 24 h reaction time and 350 rpm stirring speed in the presence of Ce-La-Zr-O and HT-500 catalysts. It is evident from the reusability study that Ce-La-Zr-O and HT-500 catalysts could be reused several times without any significant loss in their catalytic activity.

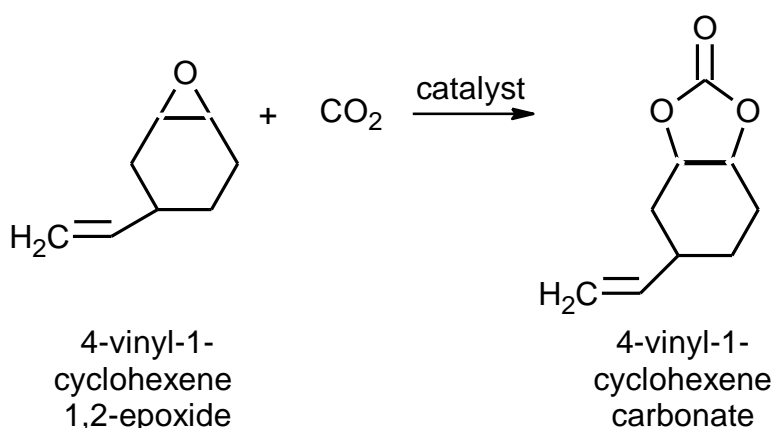
## ***CHAPTER 7***

### ***SYNTHESIS OF 4-VINYL-1- CYCLOHEXENE CARBONATE (VCHC)***

## 7. SYNTHESIS OF 4-VINYL-1-CYCLOHEXENE CARBONATE (VCHC)

### 7.1. Introduction

Synthesis of 4-vinyl-1-cyclohexene carbonate (VCHC) from cycloaddition reaction of 4-vinyl-1-cyclohexene 1,2-epoxide (VCHE) and  $\text{CO}_2$  has been investigated using novel heterogeneous catalysts (Ce-La-Zr-O and HT-500) in the absence of any organic solvent. The reaction scheme is shown in Figure 7.1. VCHC finds applications as additives, plasticizers, antifoam agent for antifreezing (Lee *et al.*, 2008). The addition reactions of VCHE and  $\text{CO}_2$  were performed in a 25 mL stainless steel high pressure reactor equipped with a thermocouple and a mechanical stirrer. Effect of different catalysts, catalyst loading,  $\text{CO}_2$  pressure, reaction temperature and reaction time was investigated to optimise the reaction condition.



**Figure 7.1.** Reaction scheme of 4-vinyl-1-cyclohexene carbonate synthesis from cycloaddition reaction of 4-vinyl-1-cyclohexene 1,2-epoxide and carbon dioxide.

### 7.2. Experimental Methods

#### 7.2.1. Chemicals

Acetone (99%) and *iso*-octane (99.8%) were purchased from Fisher Scientific UK Ltd. 4-vinyl-1-cyclohexene 1,2-epoxide (99%), *n*-Pentane (99.8%) were procured from Sigma-Aldrich Co. LLC. The purity of all

chemicals was verified by gas chromatography (GC) analysis. These chemicals were used without further purification.

### 7.2.2. Catalysts

The catalysts used for this study are the same catalysts as highlighted in the section 6.2.2.

### 7.2.3. Experimental Procedure

Cycloaddition reaction of VCHE and CO<sub>2</sub> was carried out in a 25 mL mechanically stirred Parr high pressure reactor. During any given experiment, the reactor was charged with specific amount of catalyst and the limiting reactant (VCHE), followed by the same experimental procedure highlighted in the section 6.2.3.

### 7.2.4. Methods of Analysis

An auto sampler injection Shimadzu GC-2014 gas chromatography was used to analyse the sample collected from the reaction mixture of VCHE and CO<sub>2</sub>. A ramp method was employed in order to separate all the compounds present in the sample mixture. Initial temperature of the column was set at 373 K. The column temperature was held at 373 K for 5 min after the sample was injected and ramped from 373 K to 523 K at the rate of 40°C min<sup>-1</sup>. The total run time for each sample was ~10 min. The injection needle was washed twice after the sample injection using *n*-Pentane. The column temperature was cooled down to 373 K after each sample run. Internal standard method was used for quantification of all the components present in the sample mixture and *iso*-octane was used as an internal standard.

### **7.3. Synthesis of 4-vinyl-1-cyclohexene carbonate using Commercially Available Ceria, Lanthana Doped Zirconia Catalyst**

#### **7.3.1. Results and Discussion**

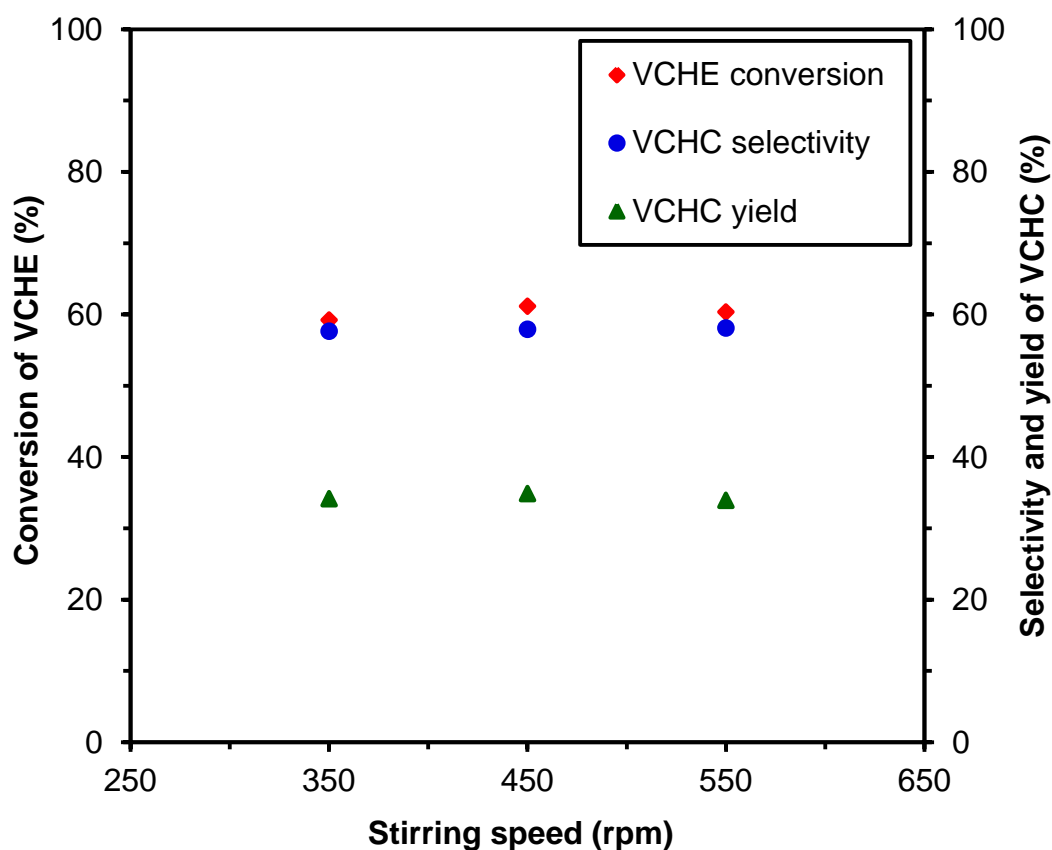
It is generally accepted that reaction parameter such catalyst loading, CO<sub>2</sub> temperature, reaction temperature and time have a significant effect on the synthesis of organic carbonate. Ce-La-Zr-O and HT-500 catalysts were adopted because of their proved good catalytic performance and high stability, to investigate the effect of reaction parameters on the synthesis of 4-vinyl-1-cyclohexene carbonate (VCHC) from addition reaction of 4-vinyl-1-cyclohexene 1,2-epoxide (VCHE) and CO<sub>2</sub>.

##### **7.3.1.1. Effect of External Mass Transfer Resistance**

Concept of mass transfer resistance in heterogeneous catalysed processes required a good understanding of physicochemical properties of the catalyst such as surface area, pore volume and particle size in order to eliminate its effect in catalytic chemical processes. In heterogeneous reaction of VCHE and CO<sub>2</sub> using a batch high pressure reactor, the effect of external mass transfer resistance on the catalytic activity of Ce-La-Zr-O catalyst was investigated at different stirring speed ranging from 350–550 rpm, and reaction conditions of 443 K temperature, 70 bar CO<sub>2</sub> pressure and 10% (w/w) catalyst loading. The results are presented in Figure 7.2. It was observed that varying stirring speed had no significant effect on the catalytic performance of Ce-La-Zr-O catalyst. As such, no significant change in the conversion of VCHE, selectivity and yield of VCHC when the reaction was conducted at different stirring speed (experimental error of  $\pm 3\%$ ). Considering the energy efficiency of the process, 350 rpm was selected for further investigation of cycloaddition reaction of VCHE and CO<sub>2</sub> to synthesise VCHC. Similar external mass transfer effect was observed for the synthesis PC from cycloaddition reaction of PO and CO<sub>2</sub> using Ce-La-Zr-O catalyst (Adeleye *et al.*, 2014). It has been reported that a decrease in catalyst particle size permits the entire surface area and pore surface area to participate in the chemical reaction. For small catalyst



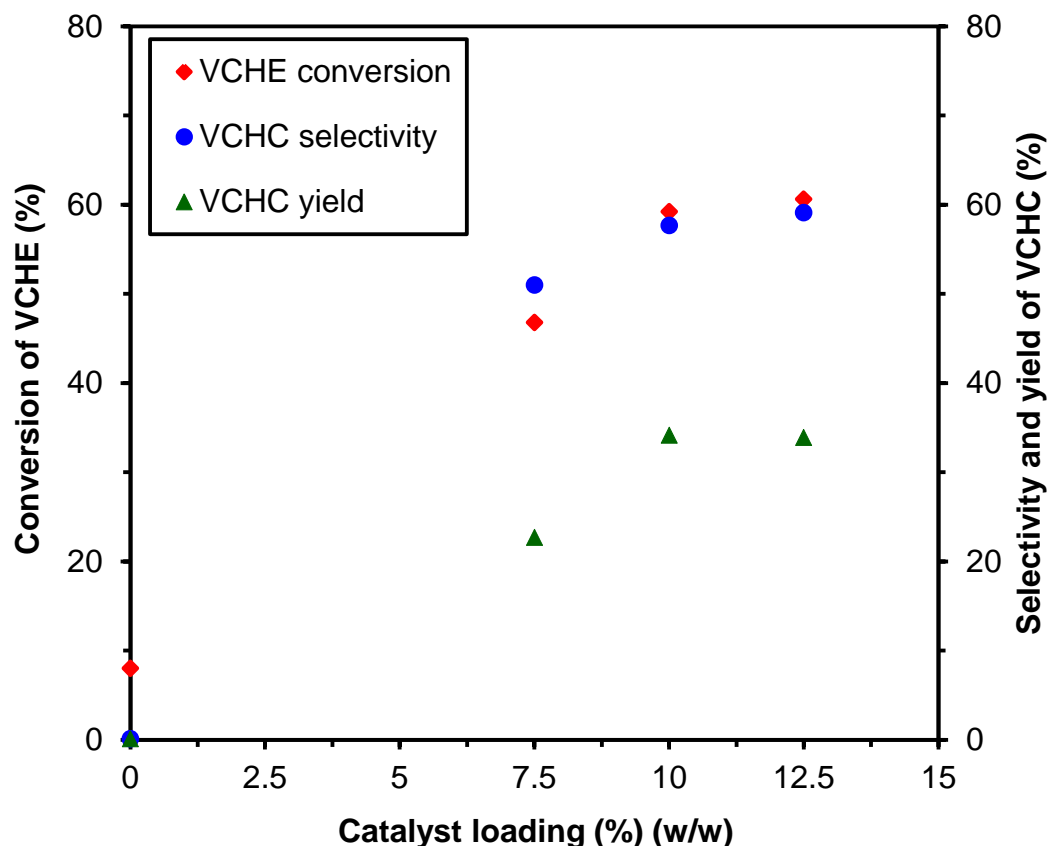
particle size (less than 255  $\mu\text{m}$ ), the reaction is chemically controlled and uninfluenced by mass transfer resistance (Adeleye *et al.*, 2014, 2015). In this case, we speculate that the effect of internal mass transfer resistance could be minimised due to the small particle size (1.7  $\mu\text{m}$ ) and average pore diameter (21.1 nm) of Ce-La-Zr-O catalysts.



**Figure 7.2.** Effect of external mass transfer resistance on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h.

#### 7.3.1.2. Effect of Catalyst Loading

Catalyst loading for the study can be defined as the percentage (%) ratio of the mass of the catalyst to the mass of the limiting reactant (VCHE). The influence of varying the catalyst loading on the yield of VCHC was investigated by conducting a set of reactions of VCHE and CO<sub>2</sub> using different amount of Ce-La-Zr-O catalyst. As shown in Figure 7.3, with an increase in Ce-La-Zr-O catalyst loading from 7.5% to 10% (w/w), there was an increase in the conversion of VCHE, selectivity and yield of VCHC from ~46% to ~59%, ~51% to ~57% and ~22% to ~34%, respectively. Further increase in catalyst loading from 10% to 12.5% (w/w) does not cause significant change ( $\pm 2$ ) in the VCHE conversion, VCHC selectivity and yield. Therefore, it was not necessary to increase the catalyst loading beyond 10% (w/w) indicating that the number of active catalytic sites for VCHC synthesis was sufficient at 10% (w/w) catalyst loading. However, control experiment (experiment conducted in the absence of Ce-La-Zr-O catalyst) shows ~8% conversion of VCHE along with no selectivity and yield of VCHC. It is obvious from the experimental results shown in Figure 7.3 that the optimum amount of catalyst required for this study is 10% (w/w).

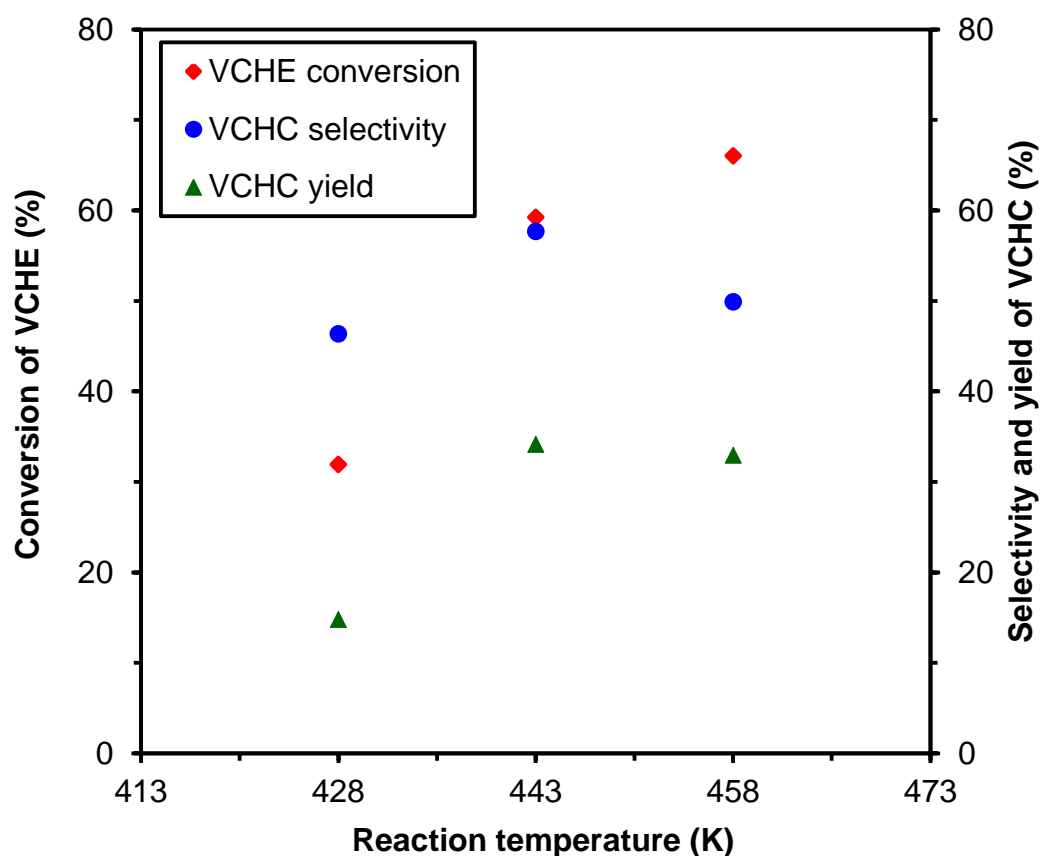


**Figure 7.3.** Catalyst loading dependence on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

### 7.3.1.3. Effect of Reaction Temperature

Figure 7.4 shows the plot of conversion of VCHE, selectivity and yield of VCHC *versus* the reaction temperature at experimental conditions of 10% (w/w) catalyst loading, 70 bar CO<sub>2</sub> pressure and 20 h reaction time. The reaction was conducted in a 25 mL high pressure reactor at varying temperature range from 428–458 K in order to study the effect of temperature for the synthesis of VCHC. It is evident from Figure 7.4 that reaction temperature has a significant effect on the synthesis of VCHC. VCHE conversion, selectivity and yield of VCHC increased from 31% to 59%, 46% to 57% and 14% to 34%, respectively, as the temperature was

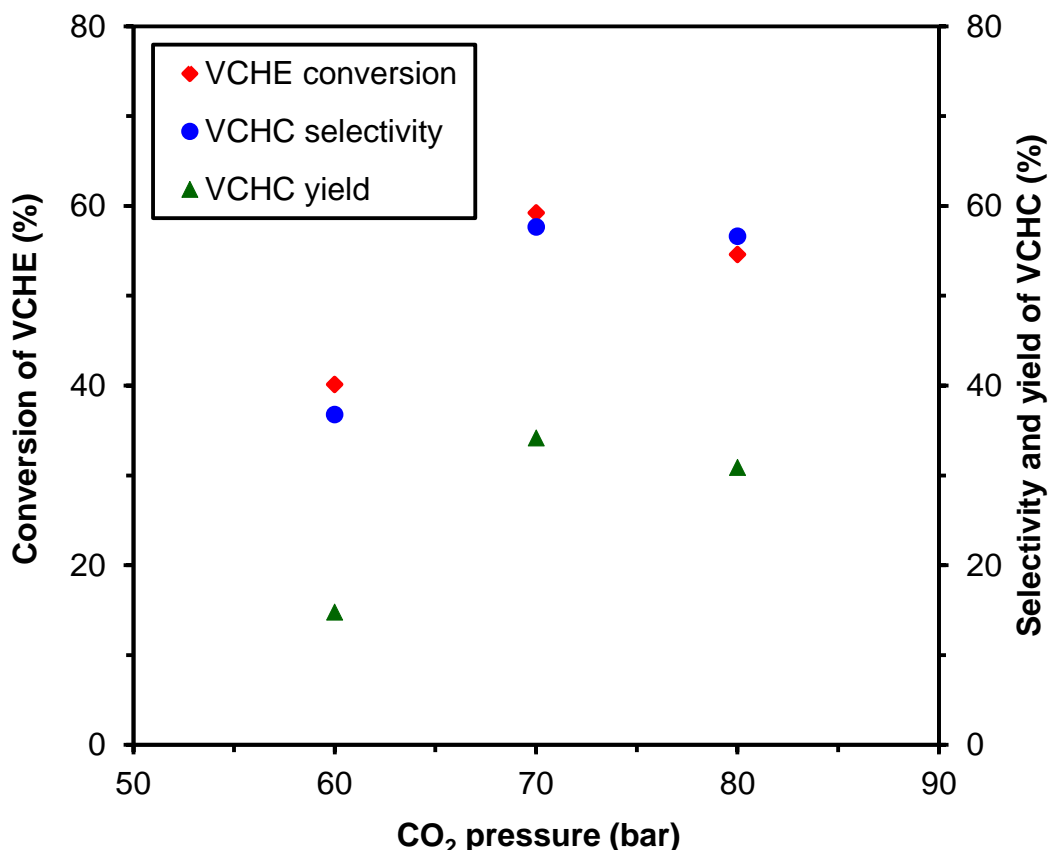
increased from 428 K to 458 K. Further increase in the temperature to 458 K resulted to a further increase in conversion of VCHE to 66%, however, decrease in the selectivity and yield of VCHC to 49% and 32%, respectively were observed. Decrease in the selectivity and yield of VCHC may be due to the decomposition of VCHE to form undesirable side products, such as isomers and dimers of VCHE at an elevated temperature of 458 K. Therefore, this study indicates that 428 K is the optimised temperature for the synthesis of VCHC from cycloaddition reaction of VCHE and CO<sub>2</sub>.



**Figure 7.4.** Temperature dependence on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

#### 7.3.1.4. Effect of Pressure

CO<sub>2</sub> pressure plays an important role in the cycloaddition reaction of VCHE and CO<sub>2</sub> for the synthesis of VCHC. It has been reported that physicochemical properties of CO<sub>2</sub> could be improved at its supercritical or near supercritical state (73.3 bar), which in turn enhances the activation of CO<sub>2</sub> molecule (Baiker, 1999; Du *et al.*, 2005; Wang *et al.*, 2006). Synthesis of VCHC *via* the reaction of VCHE and CO<sub>2</sub> was carried out between CO<sub>2</sub> pressure of 60 bar and 80 bar in order to study its effect on the synthesis of VCHC. Figure 7.5 presents the variation of VCHE conversion, selectivity and yield of VCHC at different CO<sub>2</sub> pressure and experimental condition of 443 K reaction temperature and 20 h reaction time. From Figure 7.5, it is evident that an increase in CO<sub>2</sub> pressure increases VCHE conversion, selectivity and yield of VCHC. At 70 bar CO<sub>2</sub> pressure, VCHE conversion, selectivity and yield of VCHC were ~59%, ~57% and ~34%, respectively. Further increase in CO<sub>2</sub> pressure to 80 bar gave a decrease in VCHE conversion (~54%), VCHC selectivity (~52%) and yield (~30%). Such effect of CO<sub>2</sub> pressure on catalytic activity was observed in other catalytic processes for the synthesis of organic carbonates (Kawanami and Ikushima 2000; Yasuda *et al.*, 2006). From this study, it can be concluded that the optimum CO<sub>2</sub> pressure for the reaction of VCHE and CO<sub>2</sub> using Ce-La-Zr-O is 70 bar.

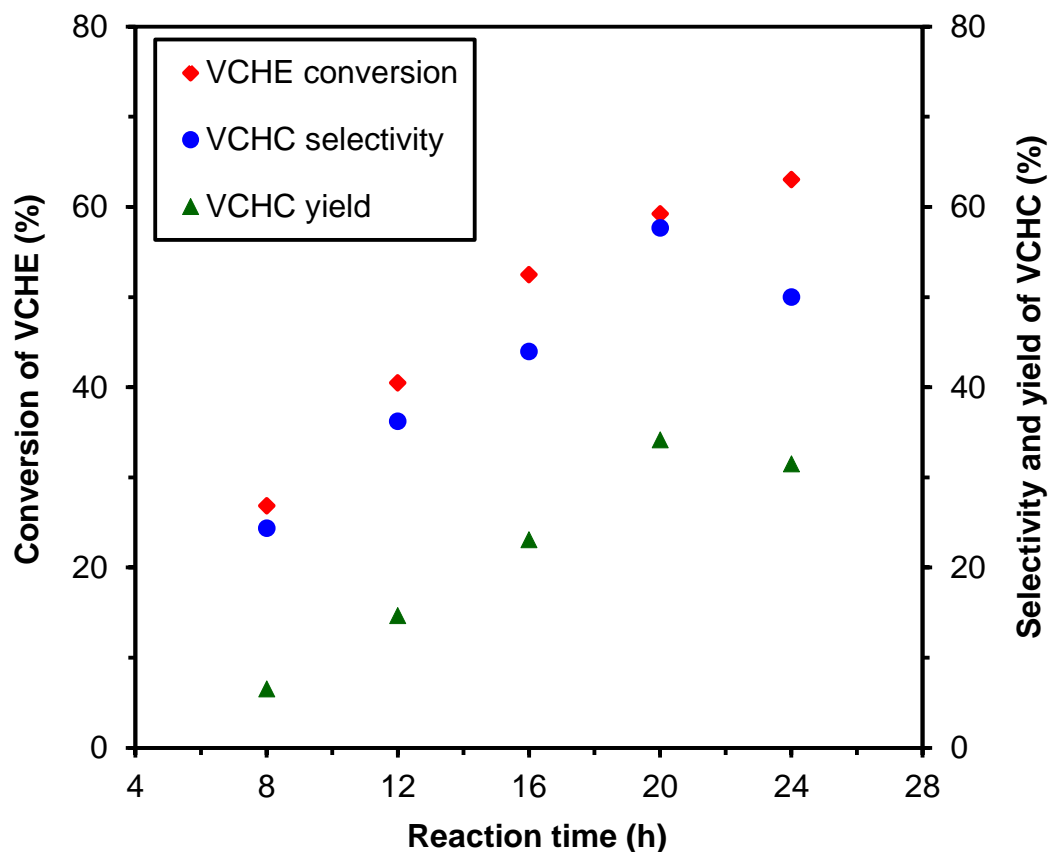


**Figure 7.5.** Pressure dependence on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; reaction time 20 h; stirring speed 350 rpm.

#### 7.3.1.5. Effect of Reaction Time

The effect of reaction time for the synthesis of VCHC was investigated to determine the optimum reaction time in the presence of Ce-La-Zr-O catalyst. The reaction was carried out in a 25 mL vessel high pressure reactor at different reaction time range from 4 h to 24 h, 443 K reaction temperature and 70 bar CO<sub>2</sub> pressure. Figure 7.6 illustrates that as reaction time was increased from 4 h to 20 h, there was an increase in VCHE conversion as well as the selectivity and yield of VCHC. VCHE conversion of ~59%, VCHC selectivity of ~57 and yield of ~34% were observed at reaction time of 20 h, When the reaction was carried out for a

longer time, i.e., 24 h, the conversion of VCHE was increased to ~63%, whereas, the selectivity and yield of VCHC were decreased to ~50% and ~31% respectively. It can be concluded that the reaction reaches equilibrium at 20 h in the presence of Ce-La-Zr-O catalyst and 20 h has been considered as the optimum reaction time for this study.

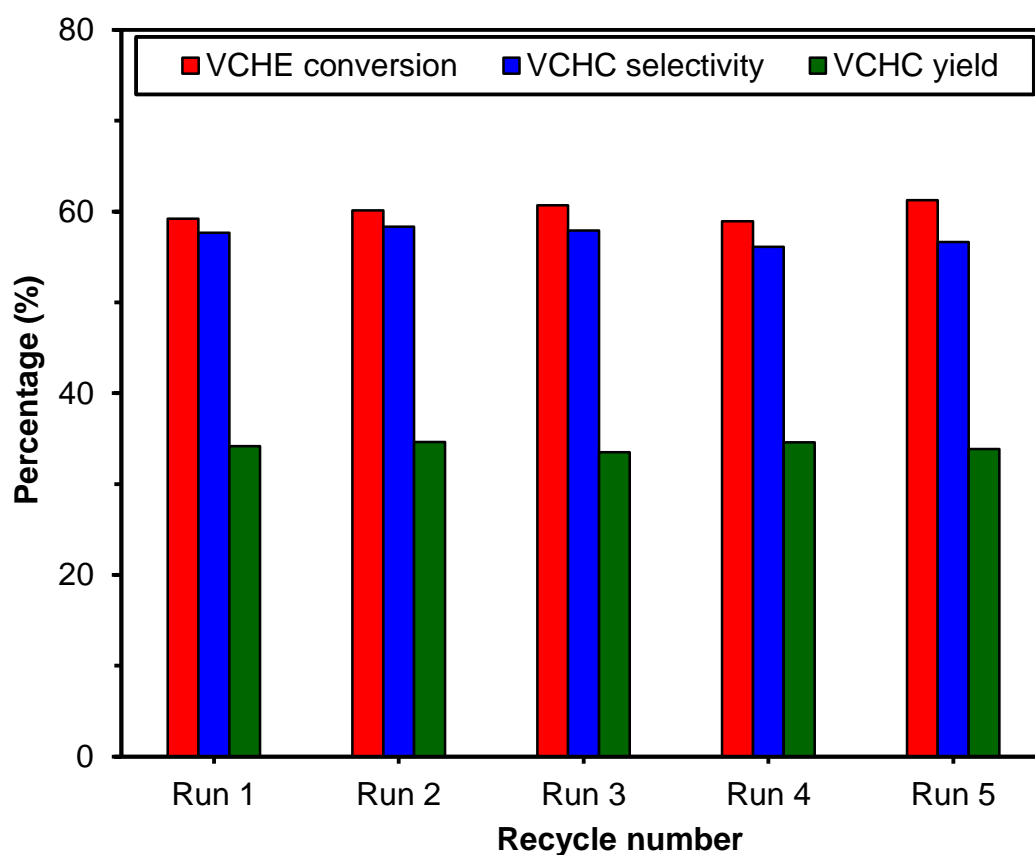


**Figure 7.6.** Time dependence on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; stirring speed 350 rpm.

#### 7.3.1.6. Catalysts Reusability Studies

Catalyst reusability studies were carried out to investigate the stability of Ce-La-Zr-O catalyst for the synthesis of VCHC. The experiments were carried out in a high pressure reactor using a fresh Ce-La-Zr-O catalyst

(10% (w/w) catalyst loading) at a reaction temperature of 443 K, CO<sub>2</sub> pressure of 70 bar and reaction time of 20 h, and plotted as Run 1 as shown in Figure 7.7. After Run 1, the catalyst was separated from the reaction mixture by filtration, washed with acetone and recovered by centrifugation. The catalyst was dried in an oven for 12 h at 353 K and reused for Run 2. The same procedure was repeated for subsequent Runs. From Figure 7.7, it was observed that there was no appreciable decrease in the VCHE conversion and yield and selectivity of VCHC after several Runs. It can be concluded that ceria and lanthana doped zirconia (Ce-La-Zr-O) catalyst exhibits an excellent reusability and stability for the synthesis of VCHC and the catalyst can be reused several times without any significant loss in its catalytic activity.



**Figure 7.7.** Catalyst reusability studies on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE), selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w);



reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

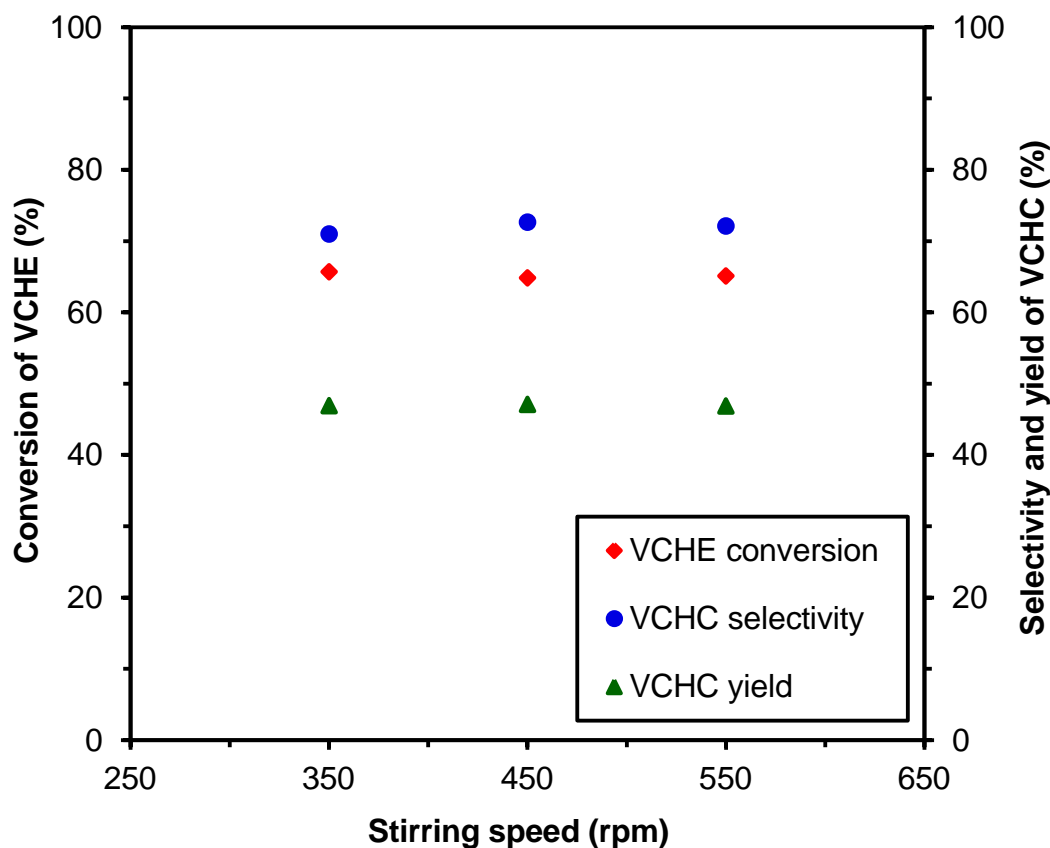
#### **7.4. Synthesis of 4-vinyl-1-cyclohexene carbonate using HT-500 (Cerium, Lanthanum and Zirconium Graphene Oxide) Catalyst**

##### **7.4.1. Results and Discussion**

The catalytic activity of mixed metal oxide cerium, lanthanum and zirconium graphene oxide (HT-500) catalyst has been investigated for the synthesis of 4-vinyl-1-cyclohexene carbonate (VCHC) in the absence of organic solvent. Effects of various parameters such as catalyst loading, CO<sub>2</sub> pressure, reaction temperature and reaction time have been studied systematically to optimise the reaction condition. Catalyst reusability studies have been conducted to investigate reusability and stability of the catalyst for the synthesis of VCHC.

##### **7.4.1.1. Effect of External Mass Transfer Resistance**

The effect of mass transfer resistance on the cycloaddition reaction of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) and CO<sub>2</sub> to produce VCHC using HT-500 was investigated in a high pressure batch reactor. The addition reactions were carried out at different stirring speed (350–550 rpm) under reaction conditions of 10% (w/w) catalyst loading, reaction temperature of 443 K, CO<sub>2</sub> pressure of 70 bar and reaction time of 20 h. The experimental results are presented in Figure 7.8. It was observed that varying stirring speed had no significant effect on the catalytic performance of HT-500 catalyst. As such, no significant change in the conversion of VCHE, selectivity and yield of VCHC were observed when the reaction was conducted at different stirring speed (experimental error of  $\pm 3\%$ ). Considering the energy efficiency of the process, 350 rpm was selected for further investigation of cycloaddition reaction of VCHE and CO<sub>2</sub> to synthesis VCHC. Similar external mass transfer effect was observed for the synthesis PC from cycloaddition reaction of PO and CO<sub>2</sub> using HT-500 catalyst (Adeleye *et al.*, 2015).

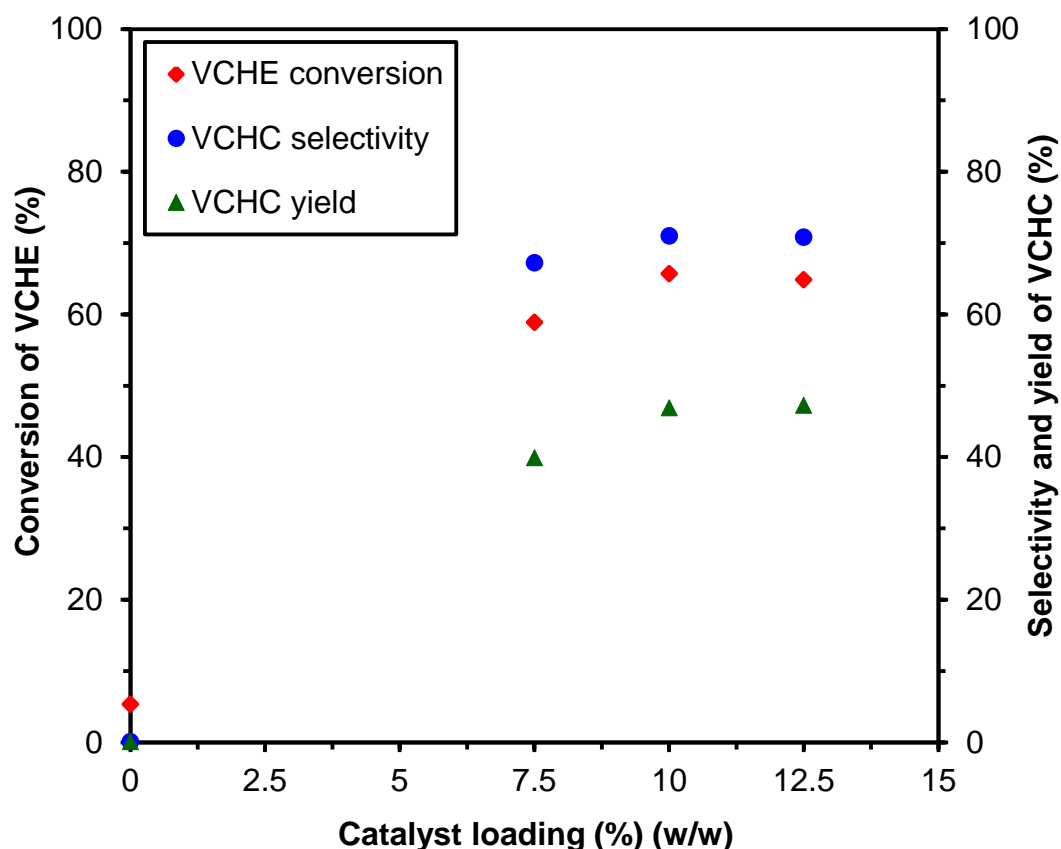


**Figure 7.8.** Effect of external mass transfer resistance on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h.

#### 7.4.1.2. Effect of Catalyst Loading

In this study, catalyst loading is defined as the percentage (%) ratio of the mass of the catalyst (HT-500) to the mass of the limiting reactant (VCHE). The influence of varying the catalyst loading on the yield of VCHC was studied by carrying out a set of cycloaddition reactions of VCHE and CO<sub>2</sub> using different amount of HT-500. The results are presented in Figure 7.9. The control experiment (reaction conducted without catalyst) gave ~5% conversion of VCHE, no selectivity and yield of VCHC were obtained. A

VCHE conversion of ~59%, VCHC selectivity of ~67% and yield of ~40% were achieved when the reaction was carried out using 7.5% (w/w) catalyst loading. An increase in the VCHE conversion to ~66%, VCHC selectivity to ~71% and yield ~46% were observed when catalyst loading increased to 10%. Similar results of VCHE conversion, VCHC selectivity and yield were achieved when the catalyst loading increased from 10% to 12.5% (w/w) and therefore, it was not necessary to increase the catalyst loading above 10% (w/w). In view of the experimental error of  $\pm 3\%$ , it seems that the number of active sites required for VCHE and CO<sub>2</sub> to react and produce VCHC was sufficient at 10% (w/w) catalyst loading. The results show that 10% (w/w) catalyst loading is the optimum amount of catalyst required for this reaction.

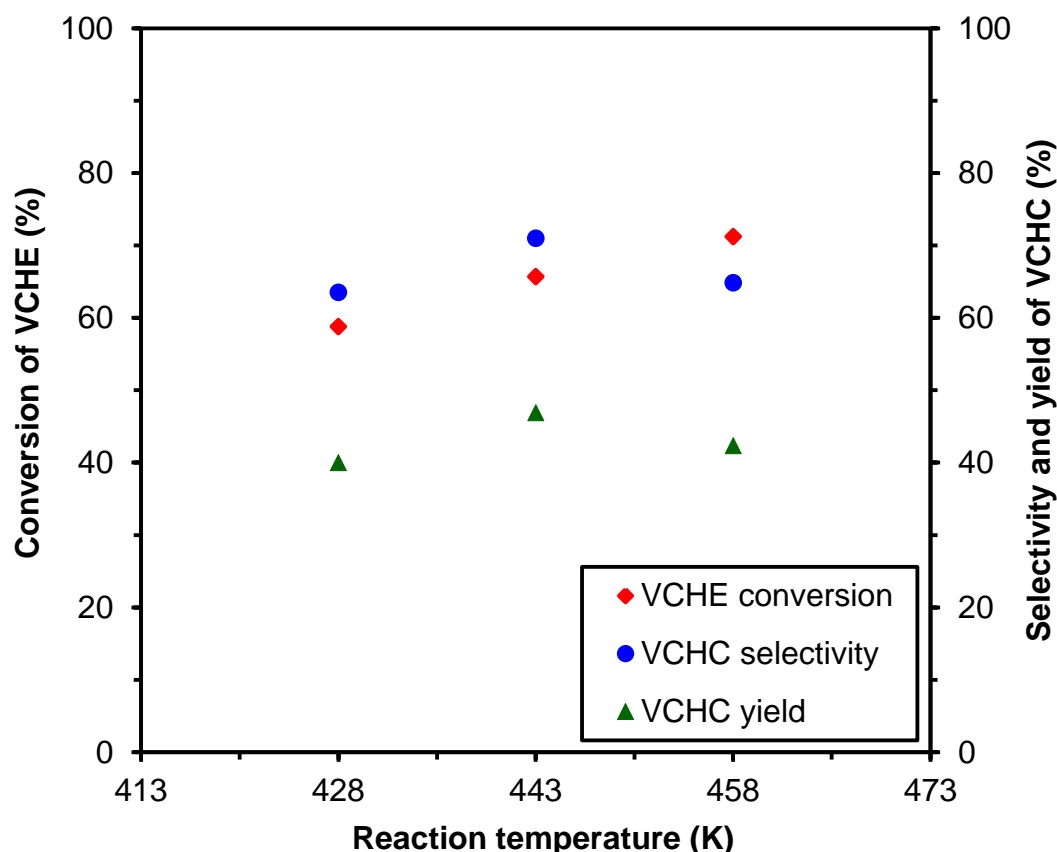


**Figure 7.9.** Catalyst loading dependence on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated

at 773 K); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

### 7.4.1.3. Effect of Reaction Temperature

An increase in reaction temperature increases the rate of reaction. Hence, experiments were conducted to study the effect of different reaction temperature on the synthesis of VCHC. Reaction temperature used for this study was 428 K, 443 K and 458 K. Figure 7.10 shows the results of the effect of temperature on the conversion of VCHE, selectivity and yield of VCHC. As the reaction temperature was increased from 428 K to 443 K, there was an increase in VCHE conversion, selectivity and yield of VCHC. At a reaction temperature of 443 K, the conversion of VCHE, selectivity and yield of VCHC were ~66%, ~71% and ~47%, respectively. Further increase in the reaction temperature to 458 K, resulted in an increase in the VCHE conversion (~71%), a decrease in the selectivity (~65%) and yield (~42%) of VCHC. The decrease in the selectivity and yield of VCHC at elevated temperature (458 K) was likely due to the formation of side products such as isomers and dimers of VCHE. Based on the experimental results, it can be concluded that 443 K was the optimum reaction temperature for this work.

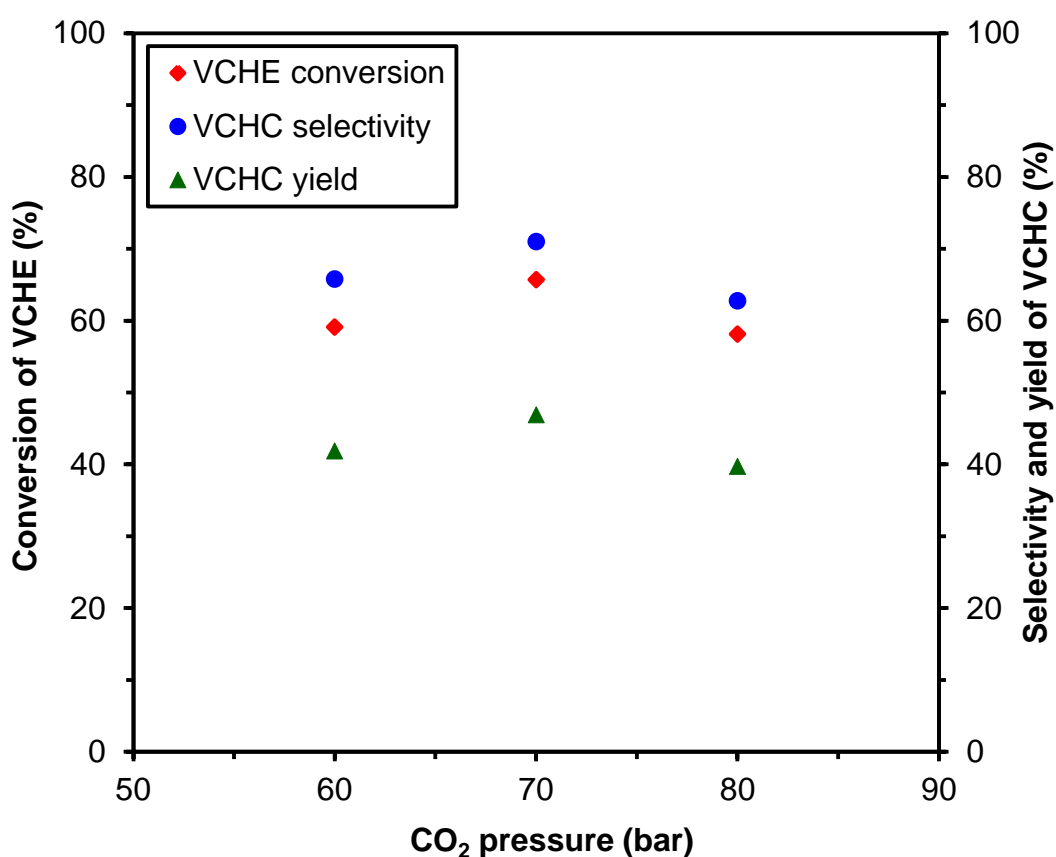


**Figure 7.10.** Temperature dependence on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

#### 7.4.1.4. Effect of CO<sub>2</sub> Pressure

Cycloaddition reaction of VCHE and CO<sub>2</sub> was carried out at varying CO<sub>2</sub> pressure to study its effect on the efficiency of VCHC synthesis. Figure 7.11 shows the CO<sub>2</sub> pressure dependence on the conversion of VCHE, selectivity and yield of VCHC. For this study, all experiments were carried out at 10% (w/w) catalyst loading and 443 K reaction temperature. It can be observed from Figure 7.11 that an increase in CO<sub>2</sub> pressure increases VCHE conversion and VCHC selectivity and yield. At 70 bar CO<sub>2</sub> pressure, VCHE conversion, selectivity and yield of VCHC were ~65%, ~71% and

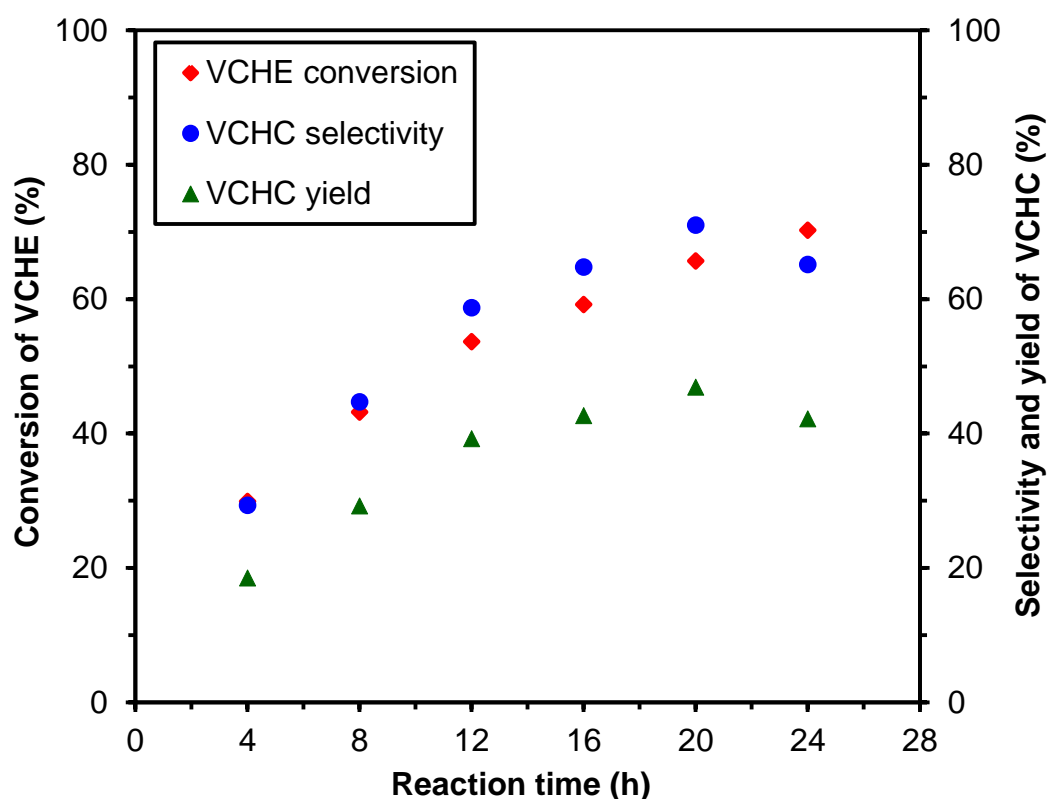
~47%, respectively. Further increase in CO<sub>2</sub> pressure to 80 bar gave a decrease in VCHE conversion (~58%), VCHC selectivity (~40%) and selectivity (~62%). Similar CO<sub>2</sub> pressure effects are often observed for several other catalyzed systems using CO<sub>2</sub> pressure in its supercritical or near supercritical state of 73.3 bar (Kawanami *et al.* 2000; Yasuda *et al.* 2006). In this work, the optimum conversion was obtained at a CO<sub>2</sub> pressure of 70 bar, and all further experiments for the synthesis of VCHC were conducted at 70 bar CO<sub>2</sub> pressure.



**Figure 7.11.** Pressure dependence on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); reaction temperature 443 K; reaction time 20 h; stirring speed 350 rpm.

#### 7.4.1.5. Effect of Reaction Time

A series of experiments were carried out at varying reaction time range from 4–24 h using HT-500 catalyst at 443 K reaction temperature and CO<sub>2</sub> pressure of 70 bar. The reaction was carried out in a 25 mL high pressure reactor. Figure 7.12 demonstrated the dependence of VCHE conversion, VCHC selectivity and yield on reaction time. Steady increase in the conversion of VCHE, selectivity and yield of VCHC was observed as the reaction time was increased from 4 h to 20 h. ~66% Conversion of VCHE, ~71% selectivity and ~67% yield of VCHC was achieved at 20 h reaction time. However, higher VCHE conversion (~70%), lower VCHC selectivity (~65%) and slight decrease in the yield (42%) of VCHC were achieved at 24 h reaction time considering the experimental error of  $\pm 3\%$ . Based on the experimental results, it can be concluded that 20 h reaction time was the optimum reaction time and all the subsequent experiments for the VCHC synthesis were performed at 20 h reaction time.



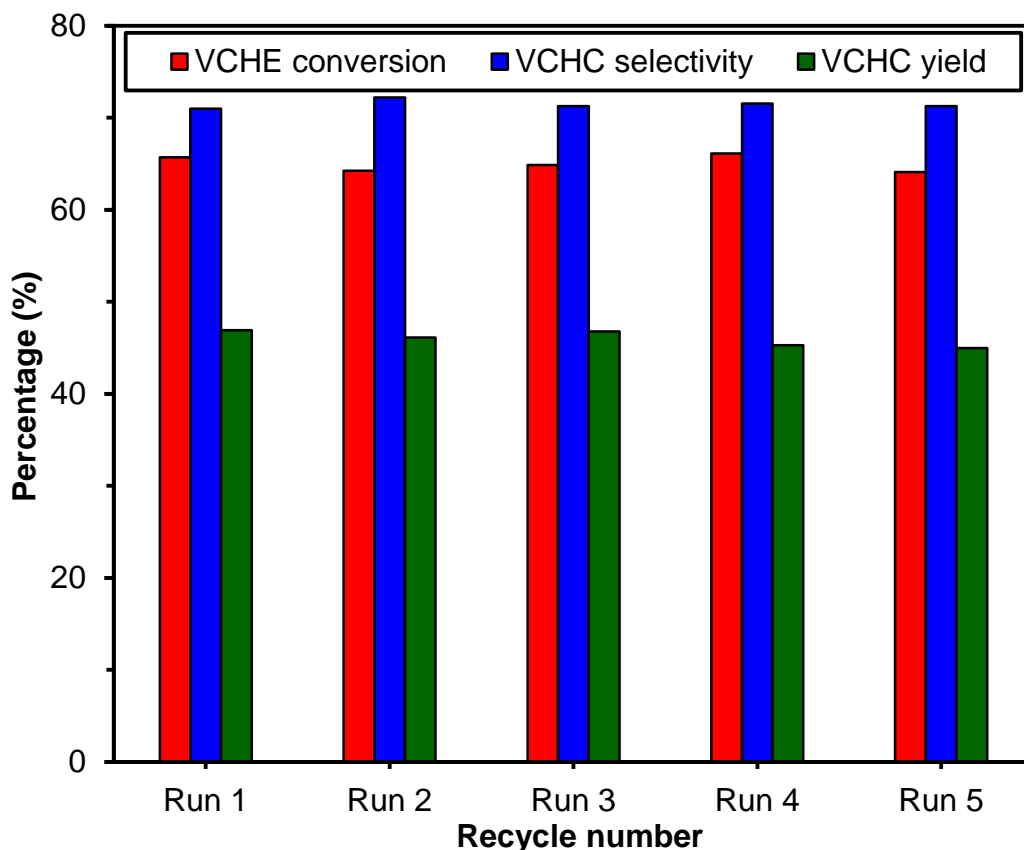
**Figure 7.12.** Time dependence on the conversion of 4-vinyl-1-cyclohexene 1, 2-epoxide (VCHE) *versus* selectivity and yield of 4-vinyl-1-

cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; stirring speed 350 rpm.

### 7.4.1.6. Catalysts Reusability Studies

Reusability studies were performed to investigate the long term stability of HT-500 catalyst at the optimum reaction conditions obtained from the batch studies, i.e. 443 K reaction temperature, 70 bar CO<sub>2</sub> pressure, 20 h reaction time and 10% (w/w) catalyst loading. The HT-500 catalyst recovered from the batch study at optimum reaction condition (Run 1) was washed three times with acetone, dried in an oven for 12 h at 353 K and reused (Run 2). The same procedure was repeated for subsequent reactions at the same reaction conditions (Run 3–5). The results are presented in Figure 7.13. It is very interesting to see that there was no significant change in results (VCHE conversion, VCHC selectivity and yield) as compared to the fresh catalyst (Run 1), indicating that HT-500 can be reused more than 5 times without any significant loss in its catalytic activity.





**Figure 7.13.** Catalyst reusability studies on the conversion of vinyl-1-cyclohexene 1, 2-epoxide (VCHE), selectivity and yield of 4-vinyl-1-cyclohexene carbonate (VCHC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 10% (w/w); reaction temperature 443 K; CO<sub>2</sub> pressure 70 bar; reaction time 20 h; stirring speed 350 rpm.

## 7.5. Conclusions

Catalytic performance of Ce-La-Zr-O and HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K) catalysts were successfully investigated for the synthesis of 4-vinyl-1-cyclohexene carbonate (VCHC) from cycloaddition reaction of 4-vinyl-1-cyclohexene epoxide (VCHE) and CO<sub>2</sub>. HT-500 showed highest catalytic performance as compared to Ce-La-Zr-O catalyst. The effect of various parameters such as the reaction time, reaction temperature, CO<sub>2</sub> pressure and catalyst loading was studied for the optimisation of VCHC synthesis. It was

found that an increase in CO<sub>2</sub> pressure resulted in an increase in the VCHE conversion, selectivity and yield of VCHC. The highest conversion of ~66%, VCHC selectivity of 71% and yield of ~47% were obtained at an optimum reaction condition of 443 K reaction temperature, 70 bar CO<sub>2</sub> pressure, 10% catalyst loading, 20 h reaction time and 350 rpm stirring speed in the presence of HT-500 catalyst. Ce-La-Zr-O and HT-500 catalysts could be reused several times without any loss in their catalytic activity.

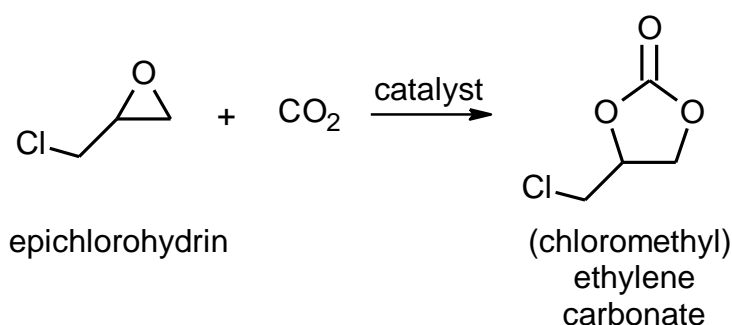
## ***CHAPTER 8***

# ***SYNTHESIS OF (CHLOROMETHYL)ETHYLENE CARBONATE (CMEC)***

## 8. SYNTHESIS OF (CHLOROMETHYL)ETHYLENE CARBONATE (CMEC)

### 8.1. Introduction

Development of heterogeneous catalytic processes for the utilisation of CO<sub>2</sub> to produce industrially useful chemicals is of growing interest in green chemical industry. (Chloromethyl)ethylene carbonate (CMEC) is one of the valuable chemicals synthesised *via* the cycloaddition of epichlorohydrin (ECH) and CO<sub>2</sub> (Figure 8.1). CMEC has found an extensive use as agricultural chemicals such as pesticides, insecticides, disinfectants and herbicides (Shaikh and Sivaram, 1996). It is used as an important intermediate for production of several chemicals such as hydroxymethyl carbonate (glycerine carbonate), used in cosmetics, personal care and medicinal applications (Huntsman corporation, 2010), methoxymethyl carbonate and phenoxymethyl carbonate (Dibenedetto *et al.*, 2011). The synthesis of CMEC *via* cycloaddition reactions of ECH and CO<sub>2</sub> was investigated in a 25 mL stainless steel high pressure reactor using Ce-La-Zr-O and HT-500 catalysts. The effect of catalyst loading, CO<sub>2</sub> pressure, reaction temperature and time was investigated to optimise the reaction conditions for the synthesis of CMEC.



**Figure 8.1.** Reaction scheme of (chloromethyl)ethylene carbonate synthesis from cycloaddition reaction of epichlorohydrin and carbon dioxide.

## **8.2. Experimental Methods**

### **8.2.1. Chemicals**

Acetone (99%) and methanol (99.9) were purchased from Fisher Scientific UK Ltd. Epichlorohydrin (99.5%), (chloromethyl)ethylene carbonate (99%) and *n*-Pentane (99.8%) were procured from Sigma-Aldrich Co. LLC. The purity of all chemicals was verified by gas chromatography (GC) analysis. These chemicals were used without further purification.

### **8.2.2. Catalysts**

The catalysts used for this study are the same as the catalysts highlighted in the section 6.2.2.

### **8.2.3. Experimental Procedure**

In a typical experiment, 25 mL high pressure reactor was charged with specific amount of catalyst and the limiting reactant (ECH), followed by the same experimental procedure highlighted in the section 6.2.3.

### **8.2.4. Methods of Analysis**

Shimadzu GC-2014 gas chromatography was used to analyse the sample collected from reaction mixture of cycloaddition reaction of ECH and CO<sub>2</sub>. A ramp method was used to separate all the compounds present in the sample mixture. Initial temperature of the column was set at 323 K. The column temperature was held at 323 K for 5 min after the sample was injected and ramped from 323 K to 593 K at the rate of 25°C min<sup>-1</sup>. The total run time for each sample was ~17 min. The injection needle was washed twice after the sample injection using *n*-Pentane. The column temperature was cooled down to 323 K after the sample run. Internal standard method was used for quantification of all the components present in the sample mixture and methanol was used as an internal standard.

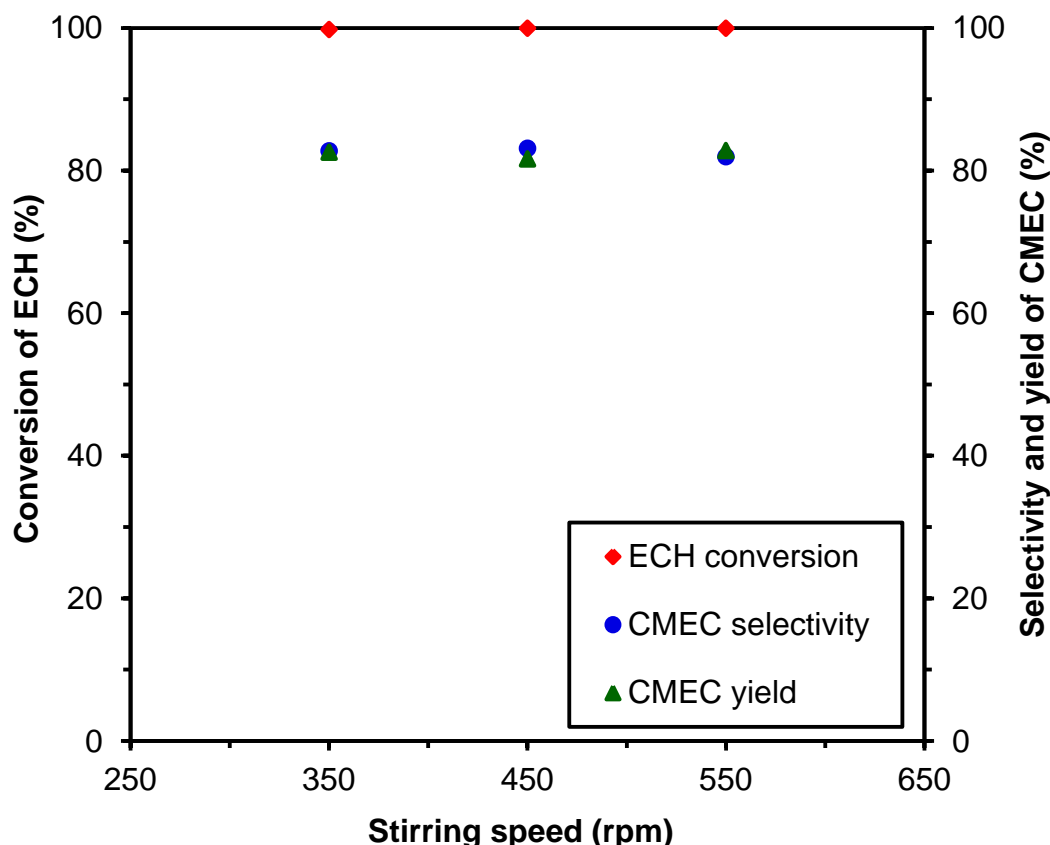
### **8.3. Synthesis of (Chloromethyl)ethylene Carbonate using Commercially Available Ceria, Lanthana Doped Zirconia Catalyst**

#### **8.3.1. Results and Discussion**

Effect of reaction parameters such catalyst loading, CO<sub>2</sub> pressure, reaction temperature and time on the synthesis of (chloromethyl)ethylene carbonate (CMEC) *via* the addition reaction of epichlorohydrin (ECH) and CO<sub>2</sub> using Ce-La-Zr-O as a catalyst has been discussed in the following section.

##### **8.3.1.1. Effect of External Mass Transfer Resistance**

Mass transfer resistance play a significant role in the heterogeneous catalytic process of organic carbonate synthesis from cycloaddition reaction of epoxide and CO<sub>2</sub>. External and internal mass transfer limitations exist in heterogeneous catalysed reactions. External mass transfer resistance occurs across the solid-liquid interface due to the stirring of the reaction mixture whereas internal mass transfer resistance occurs in the intra-particle space due to catalyst's physical and chemical structure, particle size, pore size distribution and porosity. The effect of mass transfer resistance on the addition reaction of ECH and CO<sub>2</sub> using Ce-La-Zr-O catalyst to produce CMEC was investigated using a high pressure reactor. The reactions were carried out at different stirring speed range from 350 – 550 rpm, reaction temperature of 398 K, CO<sub>2</sub> pressure of 80 bar and reaction time of 20 h. The results are presented in Figure 8.2. It can be observed that there was no significant difference in ECH conversion, selectivity and yield of CMEC at different stirring speed which indicate that there is a homogeneous distribution of catalyst particles in the reaction mixture and hence it can be concluded that external mass transfer resistance is absent in heterogeneous catalysed reaction of CMEC synthesis in the presence of Ce-La-Zr-O catalyst.

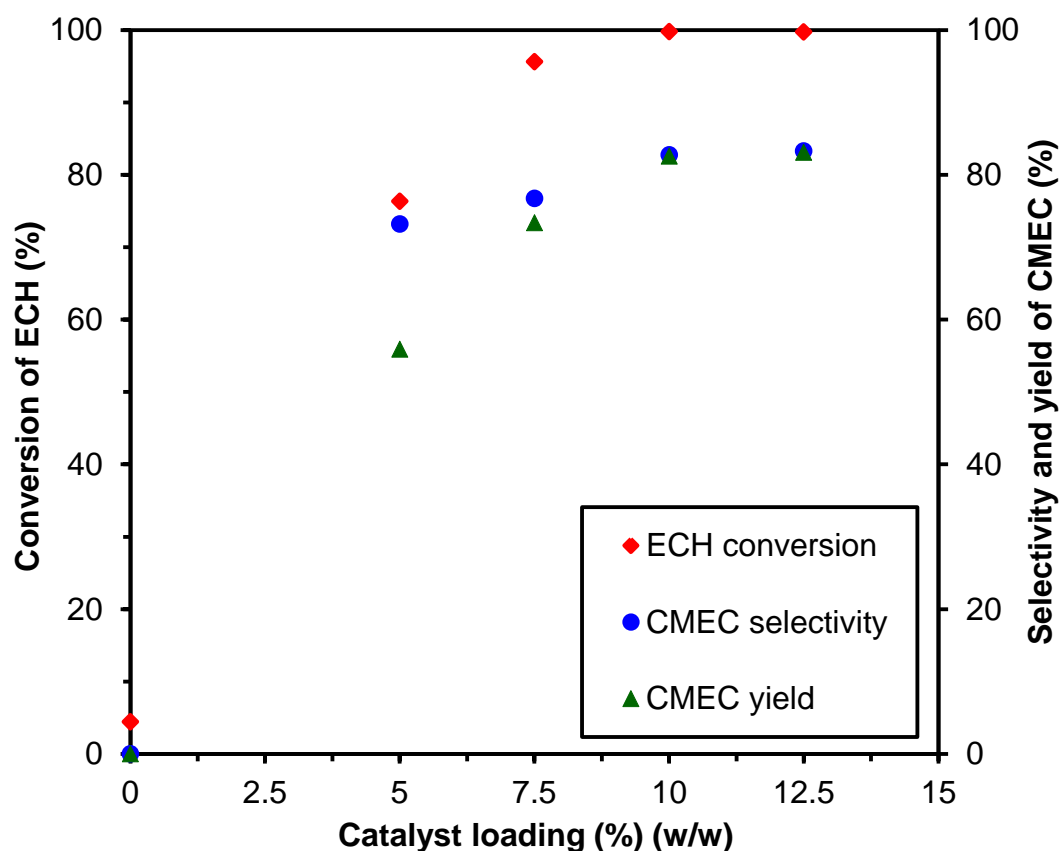


**Figure 8.2.** Effect of external mass transfer resistance on the conversion of epichlorohydrin (ECH) *versus* selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 398 K; CO<sub>2</sub> pressure 80 bar; reaction time 20 h.

#### 8.3.1.2. Effect of Catalyst Loading

The influence of catalyst loading was investigated by varying the amount of Ce-La-Zr-O catalyst to epoxide (ECH) charged into the reactor. The experiment was carried out by varying the amount of Ce-La-Zr-O catalyst from 5 to 12.5% (w/w) at 80 bar CO<sub>2</sub> pressure, 398 K reaction temperature and 20 h reaction time. Illustrated in Figure 8.3 is the effect of catalyst loading on the conversion of ECH, selectivity and yield of CMEC. The control experiment gave 4.5% conversion of ECH, however, no selectivity and yield of CMEC was observed. When the catalyst loading was

increased from 5 to 10% (w/w), steady increase in the conversion of ECH (from ~76 to ~99%), selectivity of CMEC (from ~73 to ~82%) and yield of CMEC (from ~56 to ~82%) was obtained. Further increase in the catalyst loading to 12.5% (w/w) did not show any significant increase in the conversion of ECH, selectivity and yield of CMEC. Therefore, this study indicates that 10% (w/w) is the optimised catalyst loading for the synthesis of CMEC from cycloaddition reaction of ECH and CO<sub>2</sub>.

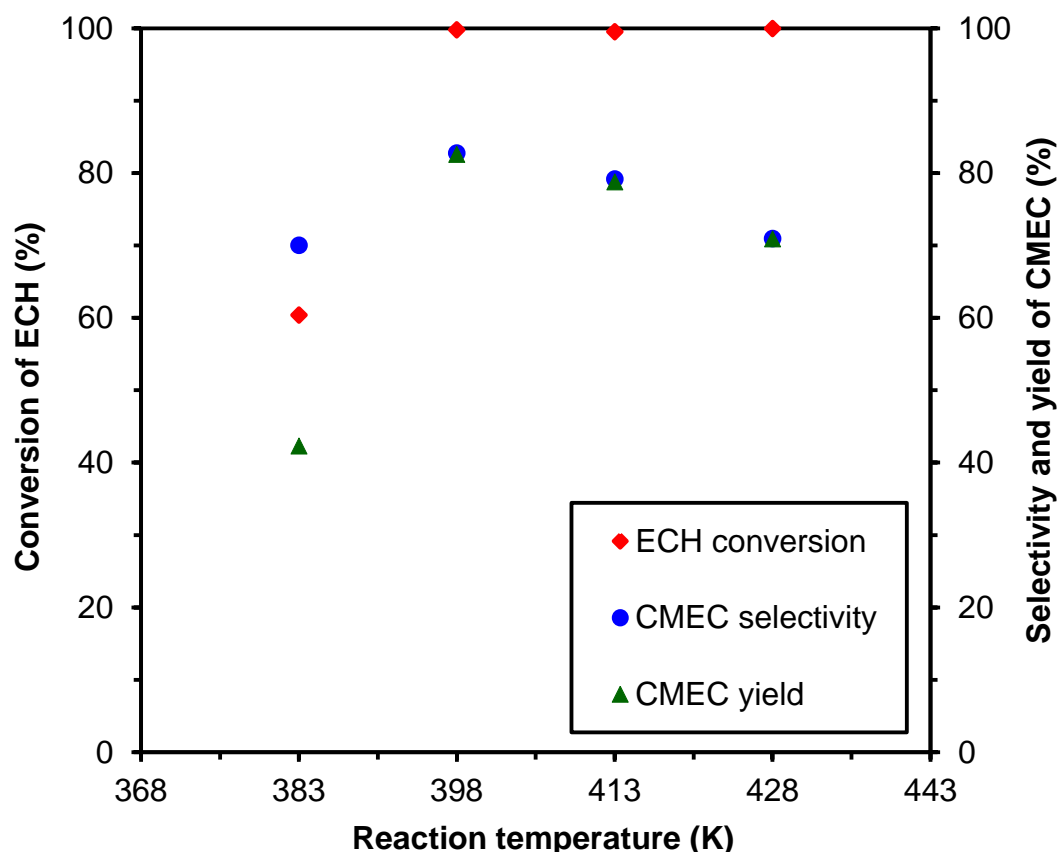


**Figure 8.3.** Catalyst loading dependence on the conversion of epichlorohydrin (ECH) *versus* selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); reaction temperature 398 K; CO<sub>2</sub> pressure 80 bar; reaction time 20 h; stirring speed 350 rpm.



#### 8.3.1.3. Effect of Reaction Temperature

The significant drawback associated with the synthesis of organic carbonates using  $\text{CO}_2$  as a reagent is the potential danger associated with operating under high temperature and high pressure. The effect of reaction temperature was studied for the synthesis of CMEC by varying the reaction temperature from 383 to 428 K. Figure 8.4 shows the experimental results for the effect of varying temperature on the synthesis of CMEC. When the reaction temperature was increased from 383 to 398 K, there was an increase in the conversion of ECH from ~60 to ~99%, selectivity of CMEC from 60 to 82% and yield of CMEC from ~42 to ~82%. The continued increase of reaction temperature beyond 398 K up to 413 K showed no change in the conversion of ECH, however, significant decrease in the selectivity and yield of CMEC were observed. Decrease in the efficiency of CMEC may be due to an increase in the formation of side products such as 3-chloropropanaldehyde and 3-chloropropanone. Therefore, 398 K was selected as optimum reaction temperature for cycloaddition reaction of ECH and  $\text{CO}_2$  to synthesise CMEC.

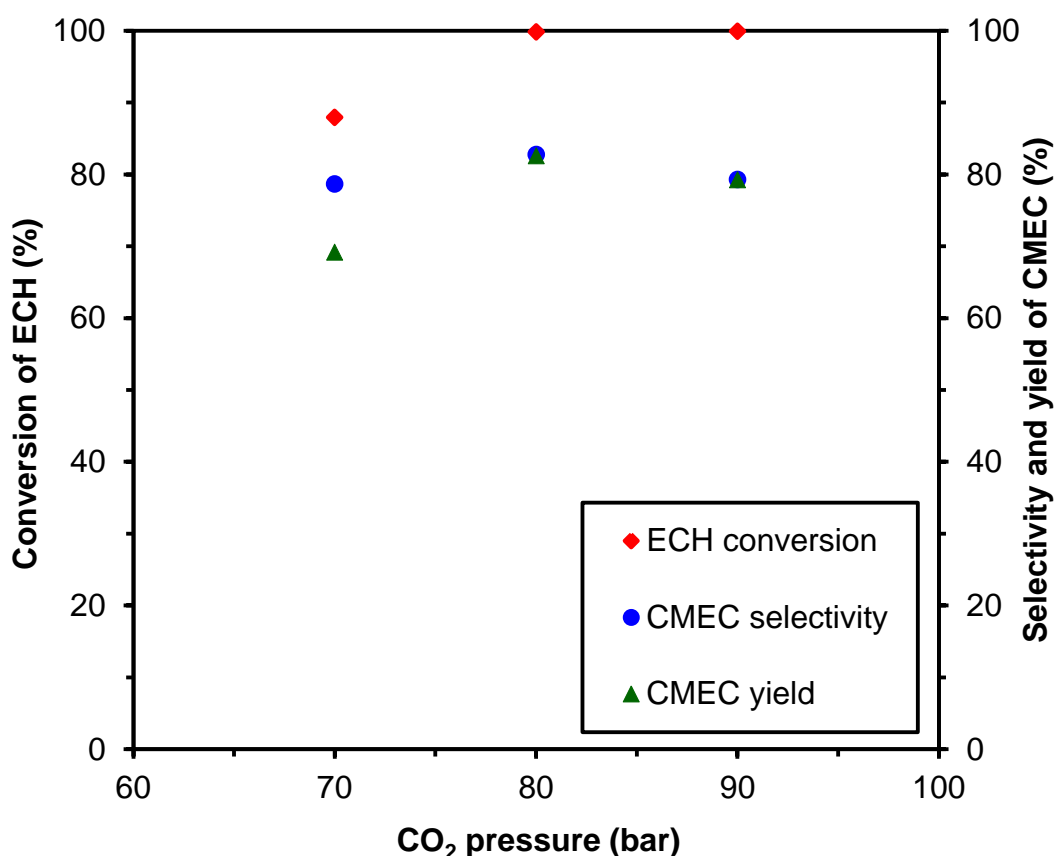


**Figure 8.4.** Temperature dependence on the conversion of epichlorohydrin (ECH) *versus* selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); CO<sub>2</sub> pressure 80 bar; reaction time 20 h; stirring speed 350 rpm.

#### 8.3.1.4. Effect of CO<sub>2</sub> Pressure

Many published literature have described the significance of CO<sub>2</sub> pressure on efficiency of organic carbonate synthesis from catalytic addition reactions of epoxides and CO<sub>2</sub>. Therefore, the optimum CO<sub>2</sub> pressure is necessary for the maximum conversion of epoxide, selectivity and yield of organic carbonate (Sun *et al.* 2009). In this work, the effect of varying CO<sub>2</sub> pressure on the synthesis of CMEC has been studied in order to determine the optimum CO<sub>2</sub> pressure at reaction conditions of 10% (w/w) catalyst loading, 398 K reaction temperature and 20 h reaction time in the

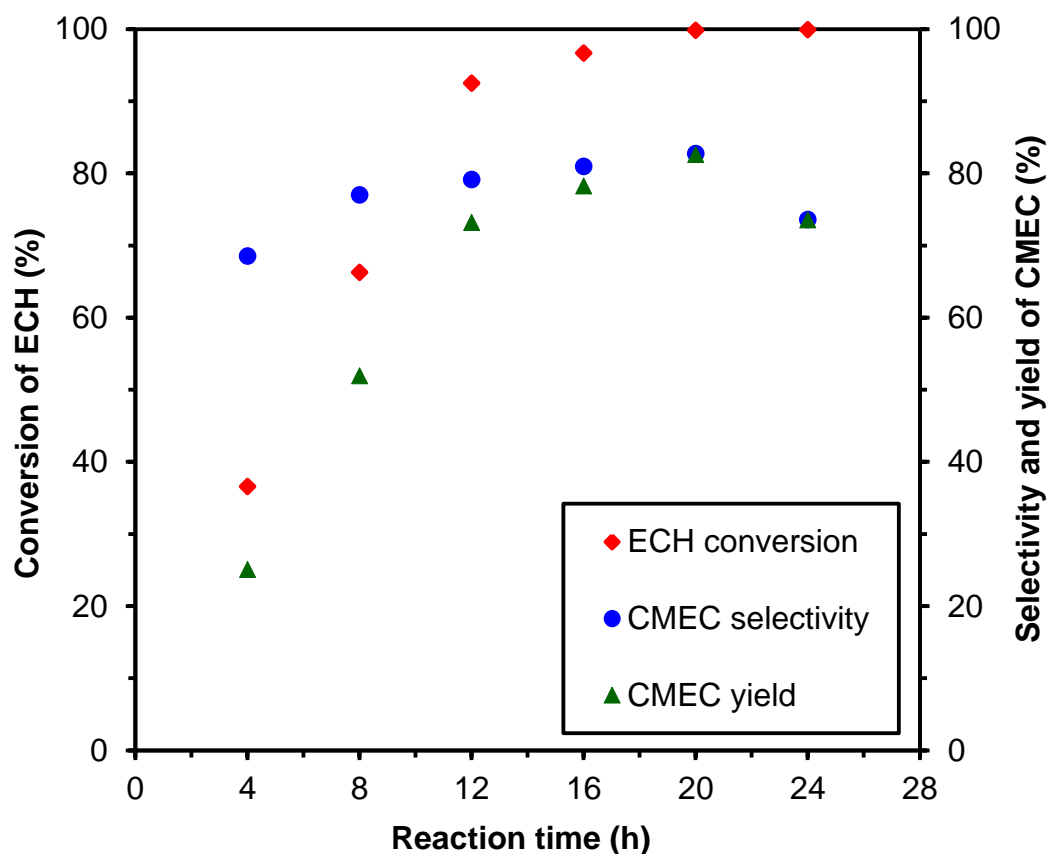
presence of Ce-La-Zr-O catalyst. The experimental results are shown in Figure 8.5. An increase in CO<sub>2</sub> pressure from 60 to 80 bar resulted in an increase in the conversion of ECH, selectivity and yield of CMEC. Cycloaddition reaction conducted at 80 bar gave ~100% conversion of ECH, ~82% selectivity and ~82% yield of CMEC, respectively. Subsequent increase in the CO<sub>2</sub> pressure to 90 bar showed no change in the conversion of ECH, but decrease in the selectivity and yield of CMEC to ~79% and ~79%, respectively were observed. For this study, 80 bar CO<sub>2</sub> pressure was considered as an optimum pressure for the synthesis of CMEC.



**Figure 8.5.** Pressure dependence on the conversion of epichlorohydrin (ECH) *versus* selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 398 K; reaction time 20 h; stirring speed 350 rpm.

### 8.3.1.5. Effect of Reaction Time

The effect of reaction time on the synthesis of organic carbonate from cycloaddition reaction of ECH and CO<sub>2</sub> has been illustrated in Figure 8.6. Reaction time investigation was carried out between 4 h and 24 h. As the time was increased from 4 to 20 h, there was a steady increase in the conversion of ECH, selectivity and yield of CMEC from ~37 to ~99%, ~68 to ~92 and ~25 to ~82%, respectively. Prolonged reaction time beyond 24 h gave no noticeable change in the conversion of ECH, however decrease to ~73% in selectivity and yield of CMEC were observed. This study showed that the optimum reaction time is 20 h using Ce-La-Zr-O as a catalyst.

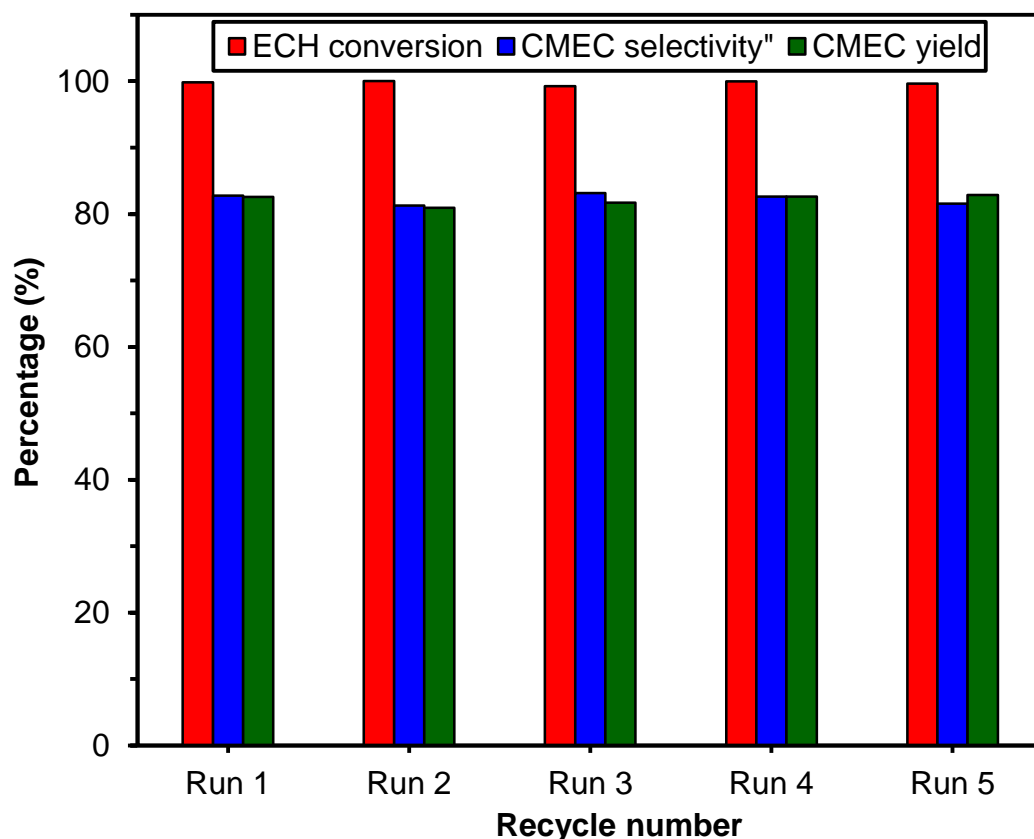


**Figure 8.6.** Time dependence on the conversion of epichlorohydrin (ECH) *versus* selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia

(Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 398 K; CO<sub>2</sub> pressure 80 bar; stirring speed 350 rpm.

#### 8.3.1.6. Catalysts Reusability Studies

Heterogeneous catalysts that could be reused several times without any significant loss in activity are generally attractive for commercial applications as most of the homogenous catalysts are very expensive and difficult to prepare. The reusability potential of Ce-La-Zr-O catalyst for cycloaddition reaction of ECH and CO<sub>2</sub> has been investigated by recycling the catalysts several times in batch studies. The results are presented in Figure 8.7. The experiments were carried out in a high pressure reactor using a fresh Ce-La-Zr-O catalyst (10% (w/w) catalyst loading) at a reaction temperature of 398 K, CO<sub>2</sub> pressure of 80 bar and reaction time of 20 h and plotted as Run 1 as shown in Figure 8.7. After Run 1, the catalyst was separated from the reaction mixture by filtration, washed with acetone and recovered by centrifugation. The catalyst was dried in an oven for 12 h at 353 K and reused for Run 2. The same procedure was repeated for subsequent Runs. It is evident from Figure 8.7 that there was no appreciable decrease in the ECH conversion, selectivity and yield of CMEC after several Runs. It can be concluded that ceria and lanthana doped zirconia (Ce-La-Zr-O) catalyst exhibits an excellent reusability and stability for the synthesis of CMEC and the catalyst can be reused several times without any significant loss in its catalytic activity.



**Figure 8.7.** Catalyst reusability studies on the conversion of epichlorohydrin (ECH), selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – ceria and lanthana doped zirconia (Ce-La-Zr-O); catalyst loading 10% (w/w); reaction temperature 398 K; CO<sub>2</sub> pressure 80 bar; reaction time 20 h; stirring speed 350 rpm.

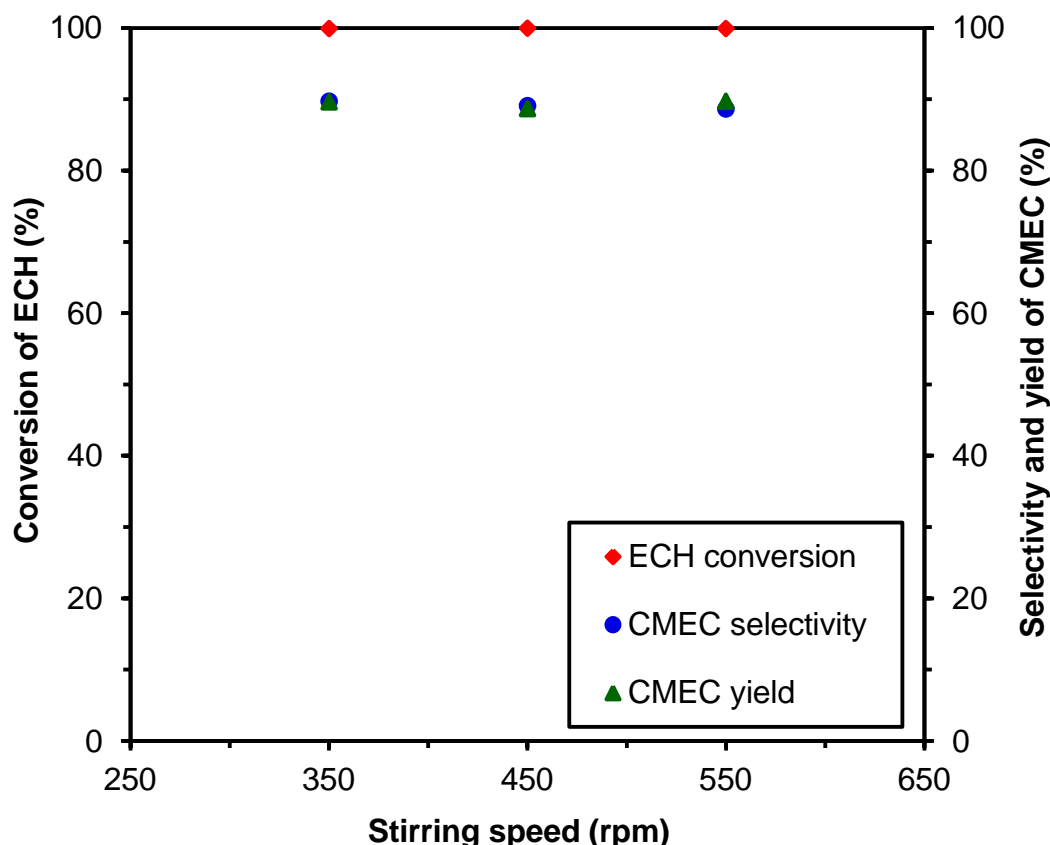
#### 8.4. Synthesis of (Chloromethyl)ethylene Carbonate using HT-500 (Ceria, Lanthana and Zirconia Graphene Oxide) Catalyst

##### 8.4.1. Results and Discussion

The formation of (chloromethyl)ethylene carbonate (CMEC) from the reaction of epichlorohydrin (ECH) and CO<sub>2</sub> using HT-500 (as prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K) as a catalyst has been studied. The effect of reaction parameters such catalyst loading, CO<sub>2</sub> temperature, reaction temperature and reaction time on the efficiency of CMEC synthesis has been discussed in the following section.

#### **8.4.1.1. Effect of External Mass Transfer Resistance**

The effect of mass transfer resistance on the cycloaddition reaction of ECH and CO<sub>2</sub> to produce CMEC using HT-500 was investigated in a high pressure batch reactor. The cycloaddition reactions were carried out at different stirring speed (350–550 rpm) under reaction conditions of 10% (w/w) catalyst loading, reaction temperature of 398 K, CO<sub>2</sub> pressure of 80 bar and reaction time of 20 h as shown in Figure 8.8. It can be observed that there were negligible difference in ECH conversion, CMEC selectivity and yield at different stirring speed, which suggest that there is a homogeneous distribution of catalyst particles in the reaction mixture and hence it can be concluded that external mass transfer resistance is absent in this study. On the other hand, HT-500 particles are fairly small, uniform and porous (mean particle size: 5.44 ± 1.39 nm and pore diameter: 2.05 nm), which eliminates mass transfer limitation. As such, it can be concluded that internal mass transfer resistance is negligible for HT-500 catalysed cycloaddition reaction due to the nature of the catalyst particles. On the basis of this investigation, all batch experiments were carried out at a stirrer speed of 350 rpm using HT-500 catalysts.



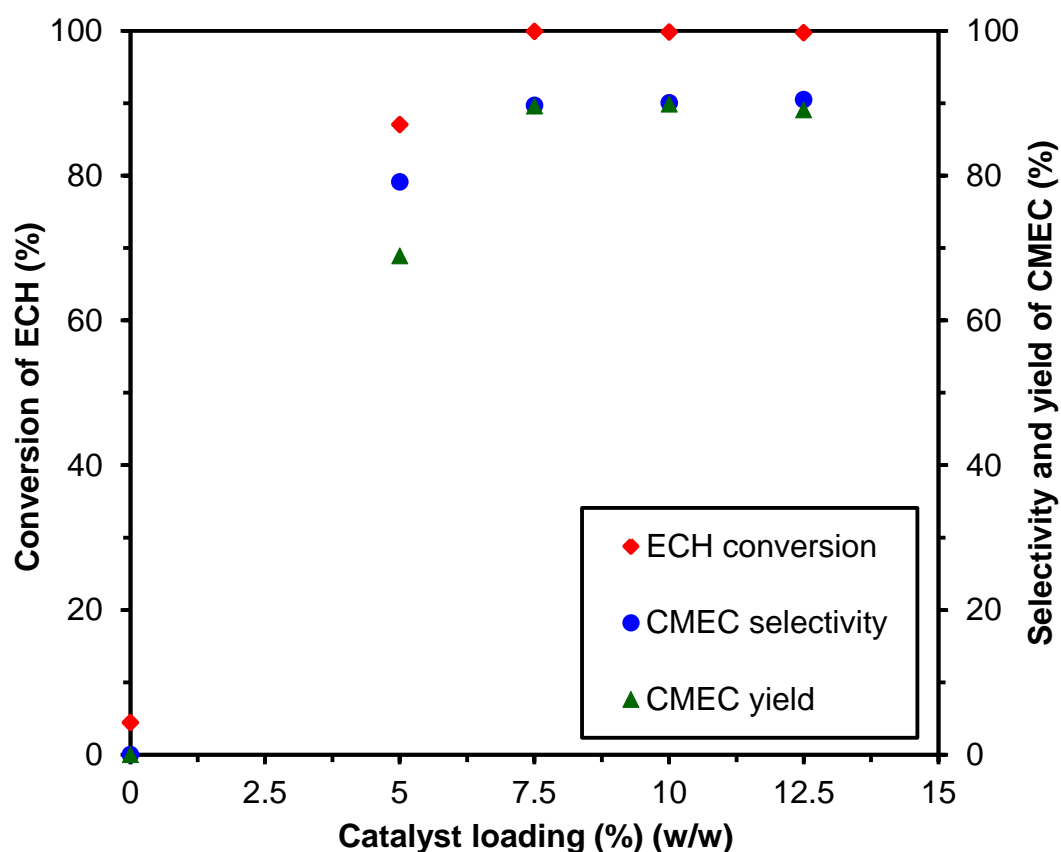
**Figure 8.8.** Effect of external mass transfer resistance on the conversion of epichlorohydrin (ECH) *versus* selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 7.5% (w/w); reaction temperature 398 K; CO<sub>2</sub> pressure 80 bar; reaction time 20 h.

#### 8.4.1.2. Effect of Catalyst Loading

One of the limitations of heterogeneous catalytic processes of cyclic carbonate synthesis is the use of high amount of catalyst. It has been found that the efficiency of CMEC synthesis was strongly affected by the amount of HT-500 catalyst as shown in Figure 8.9. The conversion of ECH, selectivity and yield of CMEC were increased as the catalyst loading was increased from 5% (w/w) to 7.5% (w/w) when the cycloaddition reaction of ECH and CO<sub>2</sub> was carried out at 398 K for 20 h. 99% conversion of ECH, ~90 selectivity and yield of CMEC were obtained at a



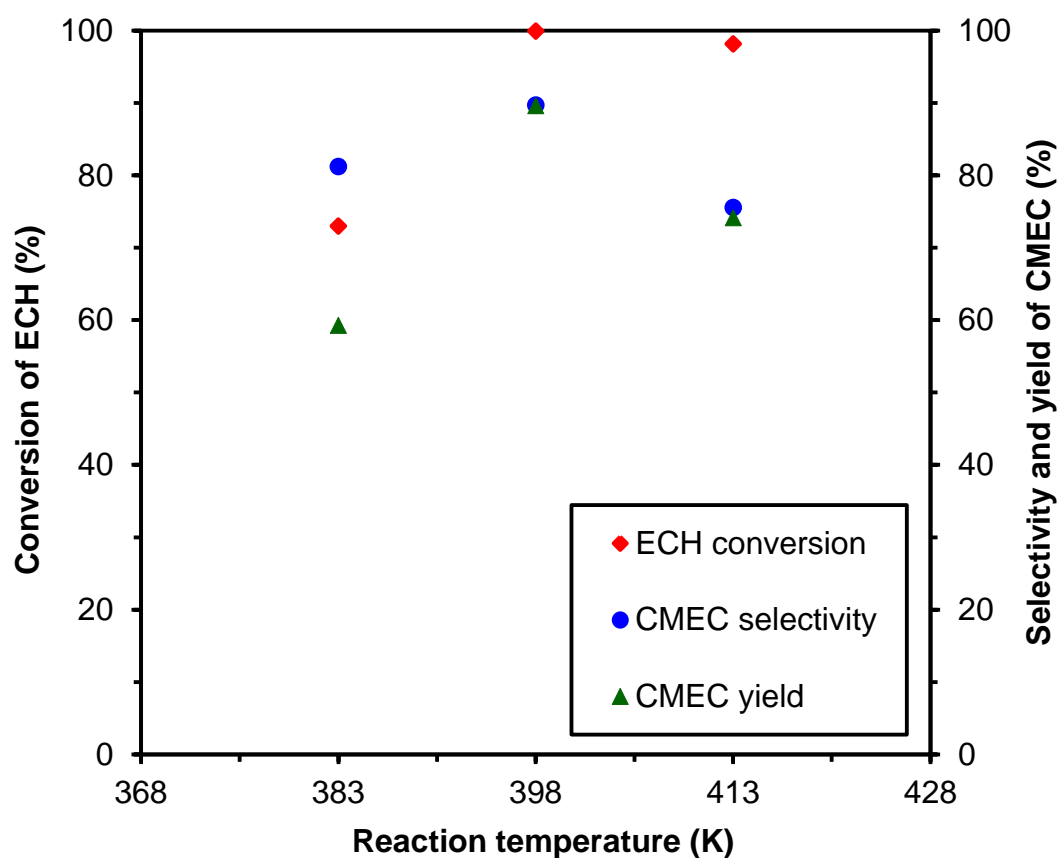
catalyst loading of 7.5% (w/w). The conversion of ECH, selectivity and yield showed no significant increase when the catalyst loading was increased beyond 7.5% up to 10% and 12.5% (w/w), respectively. Hence, there was no need to increase the catalyst loading above 7.5% (w/w). It can be concluded that 7.5% (w/w) catalyst loading is optimum for this study.



**Figure 8.9.** Catalyst loading dependence on the conversion of epichlorohydrin (ECH) *versus* selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); reaction temperature 398 K; CO<sub>2</sub> pressure 80 bar; reaction time 20 h; stirring speed 350 rpm.

#### 8.4.1.3. Effect of Reaction Temperature

It is evident from the literature that reaction temperature and CO<sub>2</sub> pressure are important parameters affecting the efficiency of cyclic carbonate synthesis from the addition reaction of epoxide and CO<sub>2</sub> (Wu *et al.*, 2008). Figure 8.10 illustrates the effect of varying temperature on the conversion of ECH, selectivity and yield of CMEC at experimental conditions of 80 bar CO<sub>2</sub> pressure for 20 h reaction time. The conversion of ECH was ~100%, CMEC selectivity was ~90% and yield was ~90% at 398 K, whereas, at 413 K, ECH conversion was ~100%, CMEC selectivity and yield were ~74% and ~76%, respectively. From this study it can be concluded that optimum temperature for the reaction of ECH and CO<sub>2</sub> using HT-500 catalyst is 398 K. Similar reaction temperatures for the synthesis of organic carbonates from epoxides and CO<sub>2</sub> have been reported in many published literature (Srivastava *et al.*, 2006; Yasuda *et al.*, 2006).

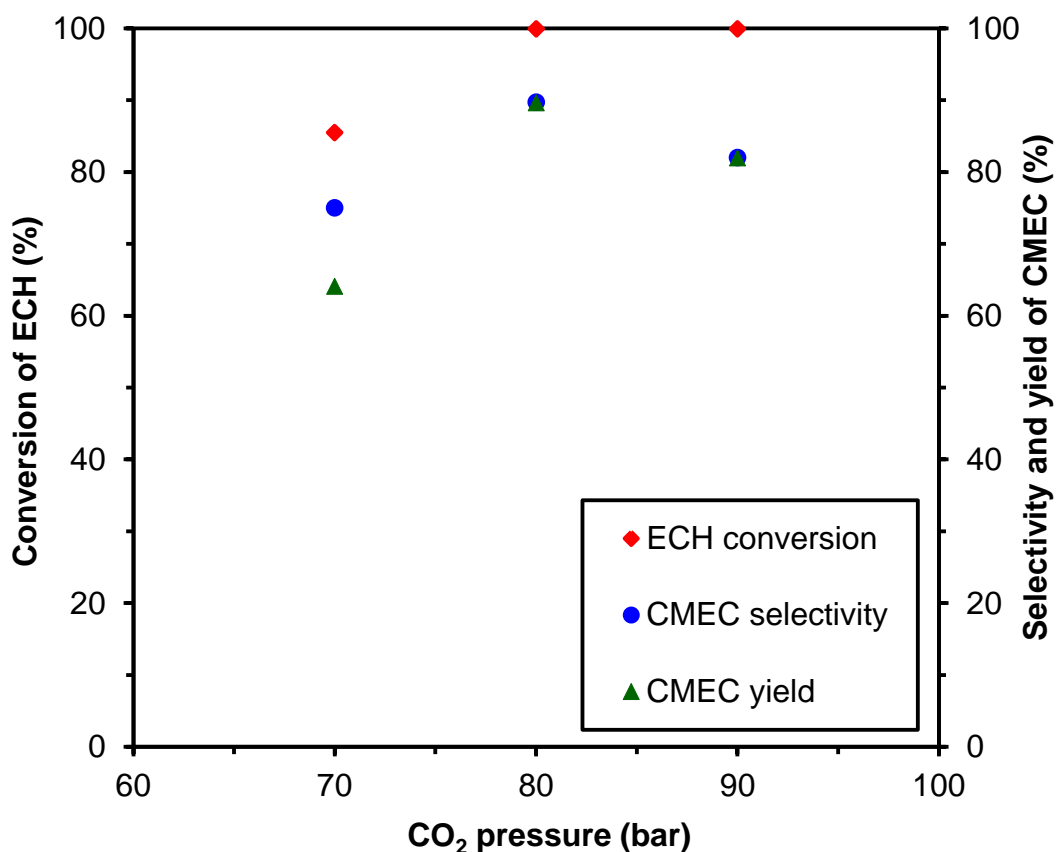


**Figure 8.10.** Temperature dependence on the conversion of epichlorohydrin (ECH) versus selectivity and yield of

(chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 7.5% (w/w); CO<sub>2</sub> pressure 80 bar; reaction time 20 h; stirring speed 350 rpm.

### 8.4.1.4. Effect of CO<sub>2</sub> Pressure

Figure 8.11 shows the effect of CO<sub>2</sub> pressure on the conversion of ECH, selectivity and yield of CMEC at reaction conditions of 398 K and 20 h using HT-500 (as-prepared Ce-La-Zr-GO catalyst heat-treated at 773 K) as a catalyst. It can be seen from Figure 8.11 that catalytic activity is higher at 80 bar CO<sub>2</sub> pressure. Hence, ~100% conversion of ECH, ~90% selectivity and ~90% yield of CMEC were achieved at 80 bar CO<sub>2</sub> pressure. Further increase in the CO<sub>2</sub> pressure from 80 to 90 bar showed no significant change in the conversion of ECH, however, a decrease in the selectivity (~81) and yield (~81%) of CMEC were obtained. Such an effect of CO<sub>2</sub> pressure on the catalytic activity has been observed in other catalytic processes for the synthesis of organic carbonates under supercritical CO<sub>2</sub> condition (Kawanami *et al.* 2000; Yasuda *et al.* 2006). This study confirmed that 80 bar CO<sub>2</sub> pressure is optimum for the reaction of ECH and CO<sub>2</sub> using HT-500 catalyst.

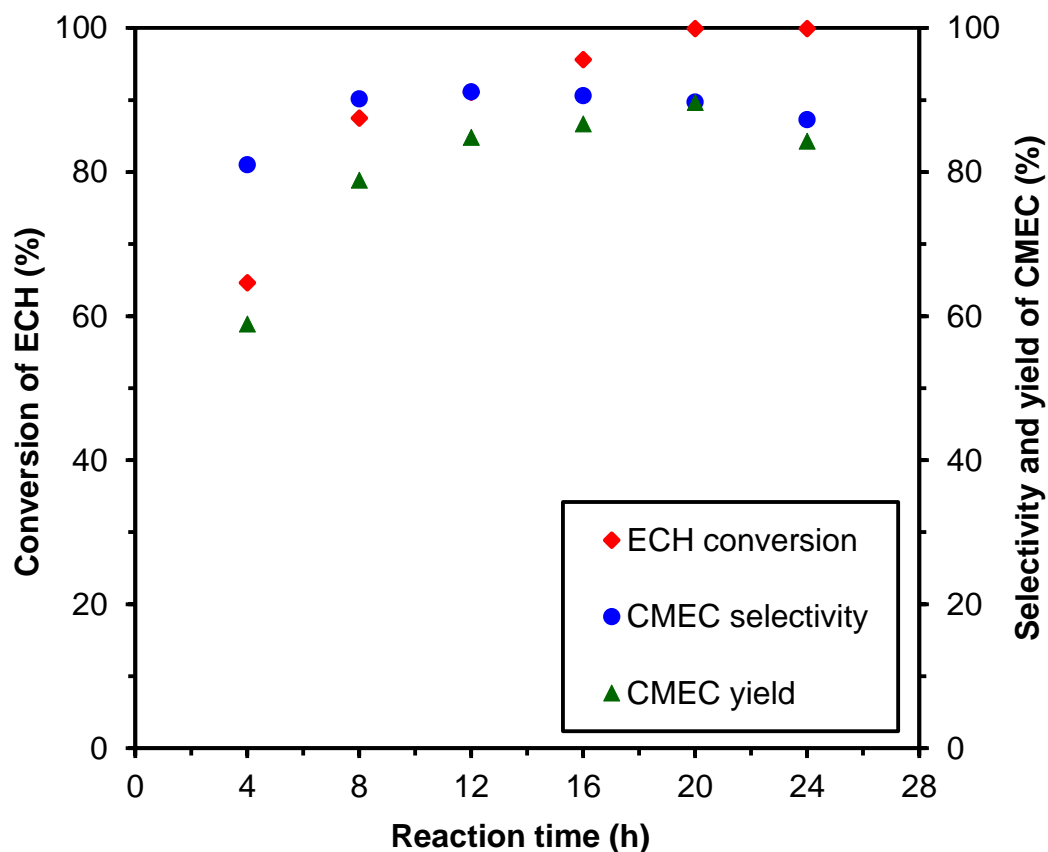


**Figure 8.11.** Pressure dependence on the conversion of epichlorohydrin (ECH) *versus* selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 7.5% (w/w); reaction temperature 398 K; reaction time 20 h; stirring speed 350 rpm.

#### 8.4.1.5. Effect of Reaction Time

The influence of varying reaction time on the synthesis of CMEC was systematically investigated by carrying out a set of cycloaddition reaction of ECH and CO<sub>2</sub> in the presence of HT-500 (as prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K) catalyst and the result is presented in Figure 8.12. ECH conversion of ~96%, CMEC selectivity of ~94% and yield of ~87% were achieved when the reaction was carried out at 16 h, which then increased to ~100%, ~90% and ~90% respectively, when the reaction was carried out at reaction time of 20 h. However,

decrease in selectivity and yield of CMEC to ~87% and ~84%, respectively, was observed at further prolonged reaction time of 24 h. In this study, 20 h is considered as optimum reaction time.

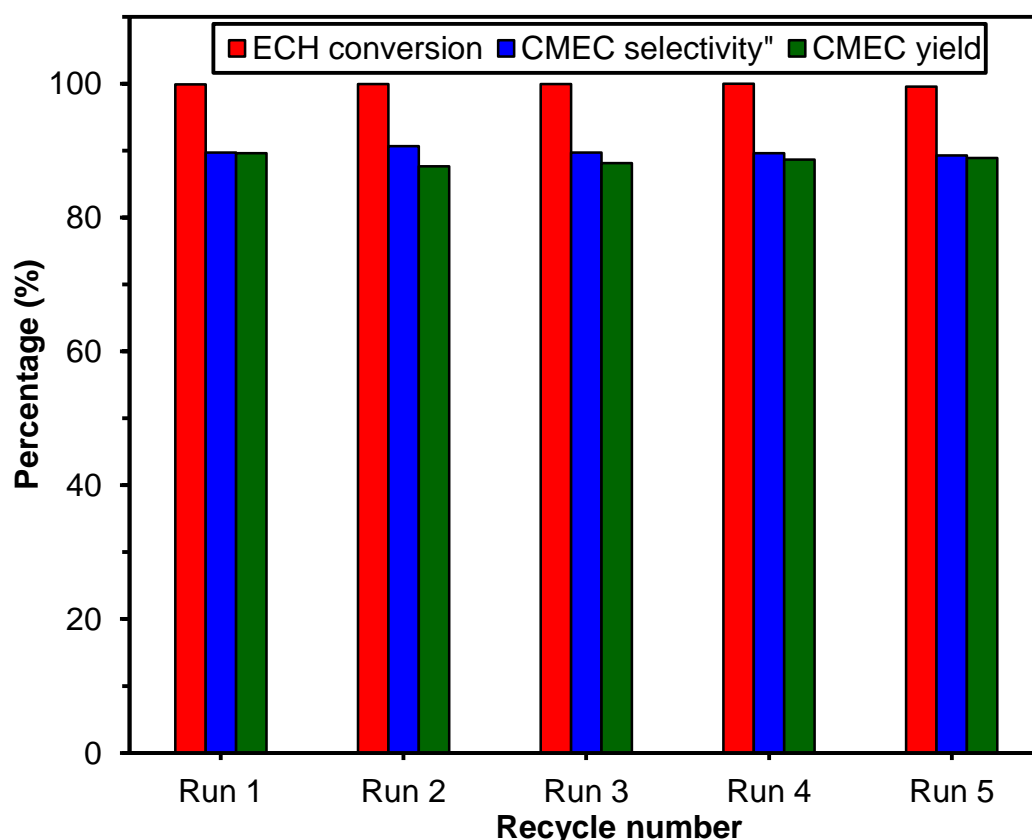


**Figure 8.12.** Time dependence on the conversion of epichlorohydrin (ECH) versus selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 7.5% (w/w); reaction temperature 398 K; CO<sub>2</sub> pressure 80 bar; stirring speed 350 rpm.

#### 8.4.1.6. Catalysts Reusability Studies

Recovery and reusability are the key factors generally limit applications of catalysts in the greener industrial processes, which include synthesis of organic carbonates from cycloaddition reaction of epoxide and CO<sub>2</sub>. HT-500 catalyst was investigated for the reusability studies, the results are

illustrated in Figure 8.13. The experiments were carried out using a fresh HT-500 catalyst (10% catalyst loading at a reaction temperature of 398 K, CO<sub>2</sub> pressure of 80 bar and reaction time of 20 h) and plotted as Run 1. After Run 1, the catalyst was separated from the reaction mixture by filtration, washed with acetone three times. The catalyst was dried in an oven for 12 h at 353 K and reused for Run 2. The same procedure was repeated for subsequent runs. It is evident from Figure 8.13, there is no significant change in the ECH conversion, selectivity and yield of CMEC after several runs considering the experimental error ( $\pm 3\%$ ). It can be concluded that ceria, lanthana and zirconia graphene oxide (HT-500) catalyst exhibited an excellent reusability and stability for the synthesis of CMEC and the catalyst can be reused several times without any significant loss in its catalytic activity.



**Figure 8.13.** Catalyst reusability studies on the conversion of epichlorohydrin (ECH), selectivity and yield of (chloromethyl)ethylene carbonate (CMEC). Experimental conditions: Catalyst – HT-500 (as-

prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K); catalyst loading 7.5% (w/w); reaction temperature 398 K; CO<sub>2</sub> pressure 80 bar; reaction time 20 h; stirring speed 350 rpm.

### 8.5. Conclusions

The cycloaddition reaction of ECH and CO<sub>2</sub> for the synthesis of CMEC was successfully conducted in a high pressure reactor using ceria, lanthana doped zirconia (Ce-La-Zr-O) and HT-500 (as-prepared ceria, lanthana and zirconia graphene oxide heat-treated at 773 K) catalysts respectively, in the absence of an organic solvent. It was found that an increase in CO<sub>2</sub> pressure resulted in an increase in the ECH conversion, selectivity and yield of CMEC. HT-500 catalyst showed high catalytic performance for CMEC synthesis as compared to other reported heterogeneous catalysts. The highest ECH conversion of ~99%, CMEC selectivity of ~90% and yield of ~90% were obtained at an optimum reaction condition of 398 K, 80 bar, 350 rpm and 20 h using 7.5% (w/w) HT-500 catalyst. The reusability studies of Ce-La-Zr-O and HT-500 catalysts were conducted to investigate the long term stability for CMEC synthesis. It was found that both catalysts could be easily separated from the reaction mixture and reused several times without any loss in the catalytic activity.

## ***CHAPTER 9***

# ***CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORKS***



## 9. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORKS

### 9.1. Conclusions

In this work, several heterogeneous catalysts have been investigated for the syntheses of cyclic organic carbonates from cycloaddition reaction of various epoxides and CO<sub>2</sub>. The experiments have been conducted in a batch high pressure reactor to systematically investigate experimental parameters affecting the efficiency of syntheses of organic carbonates. An extensive review of related literature has been presented so as to give an overview of various methods and catalysts that have been used for the production of cyclic organic carbonates.

Heterogeneous catalysts such as metal oxides, mixed metal oxides and graphene-inorganic nanocomposite catalysts were prepared using a continuous hydrothermal flow synthesis (CHFS) reactor. Graphene oxide (GO) was prepared using improved method by Hummers and Offerman, (1958). Graphene oxide is a novel support widely used in several heterogeneous catalytic applications. Characterisation of all the catalysts including commercially available ceria and lanthana doped zirconia (Ce-La-Zr-O), ceria doped zirconia (Ce-Zr-O), lanthana doped zirconia (La-Zr-O), lanthanum oxide (La-O) and zirconium oxide (Zr-O) catalysts were performed using Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), x-ray powder diffraction (XRD) and micromeritics analyser to investigate the relationship between catalytic performance and morphology, particle size, surface area and composition of the catalyst. Ceria, lanthana and zirconia graphene oxide nanocomposite catalyst synthesised using a continuous hydrothermal flow synthesis (CHFS) reactor and heat-treated at 773 K (HT-500) exhibited pore volume of 0.036 cm<sup>3</sup> g<sup>-1</sup>, BET surface area of 92 m<sup>2</sup> g<sup>-1</sup> and particle size of 5.44 nm and showed highest catalytic activity for the synthesis of propylene carbonate (PC), butylene carbonate (BC), 4-vinyl-1-cyclohexene carbonate (VCHC)

and (chloromethyl)ethylene carbonate (CMEC) as compared to other catalysts investigated as part of this work.

Synthesis of propylene carbonate (PC) from cycloaddition reaction of carbon dioxide ( $\text{CO}_2$ ) and propylene oxide (PO) was successfully conducted in a high pressure reactor in the presence of various heterogeneous catalysts and without the use of an organic solvent. HT-500 catalyst exhibited highest catalytic activity and its performance was systematically assessed for PC synthesis. The optimum reaction condition was found at 443 K, 70 bar  $\text{CO}_2$  pressure, 10% catalyst loading, 20 h reaction time and 350 rpm stirring speed in the presence of HT-500 catalyst. The PO conversion of ~86%, PC selectivity of ~94% and yield of 82% were recorded at optimum operating conditions.

Catalytic performance of Ce-La-Zr-O and HT-500 catalysts were assessed for the synthesis of butylene carbonate (BC), 4-vinyl-1-cyclohexene carbonate (VCHC) and (chloromethyl)ethylene carbonate (CMEC) from cycloaddition reaction of their corresponding epoxides and  $\text{CO}_2$  without the use of organic solvent. HT-500 catalyst exhibited highest catalytic activity as compared to Ce-La-Zr-O catalyst. The optimum reaction condition for the synthesis of butylene carbonate (BC) was found at 443 K reaction temperature, 70 bar  $\text{CO}_2$  pressure, 10% catalyst loading, 24 h reaction time and 350 rpm stirring speed in the presence of Ce-La-Zr-O and HT-500 catalysts. BO conversion of ~88%, BC selectivity of 92% and yield of ~84% was achieved in the presence of HT-500 catalyst at optimum experimental conditions. VCHE conversion of ~66%, VCHC selectivity of 71% and yield of ~47% were obtained at an optimum reaction condition of 443 K reaction temperature, 70 bar  $\text{CO}_2$  pressure, 10% catalyst loading, 20 h reaction time and 350 rpm stirring speed in the presence of HT-500 catalyst. ECH conversion of ~100%, CMEC selectivity of ~90% and yield of ~90% were obtained at an optimum reaction condition of 398 K, 80 bar, 350 rpm and 20 h using 7.5% (w/w) HT-500 catalyst. In addition, it was

found that ECH showed higher reactivity as compared to other epoxides investigated. Hence, activity of epoxides investigated decreases in the following order: ECH > PO > BO > CHO.

The efficiency and long term stability of Ce-La-Zr-O and HT-500 catalysts have been assessed for the synthesis of organic carbonate from cycloaddition reaction of epoxides and CO<sub>2</sub> in a high pressure reactor. Series of experiments were conducted by reusing the fresh catalyst several times. It was recorded that Ce-La-Zr-O and HT-500 catalysts could be easily separated from the reaction mixture by simple filtration and reused five (5) times without noticeable loss in the catalytic activity.

### 9.2. Recommendations for Future Works

The following recommendations are suggested for future work:

#### 9.2.1. Use of Waste CO<sub>2</sub> for Organic Carbonate synthesis

Waste CO<sub>2</sub> is produced with many different impurities. The large scale of CO<sub>2</sub> is produced from flue gas power station which typically has CO<sub>2</sub> concentration of 6–13% and contains other impurities such as water vapour, nitrogen dioxide and sulphur dioxide. It would be desirable and economical to develop a technology that will directly utilise CO<sub>2</sub> from the source (flue gas) for synthesis of organic carbonates. In this process, the entire costs associate with the carbon capture and storage (CCS), purifying, concentrating and pressurising waste CO<sub>2</sub> could be avoided. Therefore, synthesis of organic carbonate could be investigated *via* the reaction of epoxide and simulated flue gas.

#### 9.2.2. Heterogeneous Catalysts

Development of efficient, highly selective, stable and reusable catalysts for cyclic carbonate synthesis is generally desirable in several industrial applications. Heterogeneous catalysts are considered to be most preferred catalysts for industrial application due to their technical advantages over

the homogenous catalysts. It would be useful to synthesise and investigate other different types of heterogeneous catalysts such as metal oxide, mixed metal oxide and graphene-inorganic nanocomposite catalysts. Heterogeneous catalysts could be investigated by varying the percentage composition of the catalyst components in order to identify the most appropriate ratio of the components that would provide an efficient heterogeneous catalyst for the syntheses of organic carbonates.

### **9.2.3. Catalyst Characterisation**

Catalytic performance of most heterogeneous catalysts is due to the cooperative action of acid-base sites derived from the formation of metal-oxygen bonds, which are significant for the activation of epoxide and  $\text{CO}_2$  to produce organic carbonates. It would be useful to investigate the redox properties of heterogeneous catalysts in order to identify appropriate combination of metal oxide and to establish the relationship between catalytic performance and acid-base properties for the synthesis of organic carbonate.  $\text{NH}_3$  temperature-programed desorption (TPD) could be used to measure acidic properties of the catalysts.

### **9.2.4. Synthesis of Other Valuable Organic Carbonates**

Other industrially important cyclic carbonates such as styrene carbonate, diphenyl carbonate, dimethyl carbonate and aliphatic carbonates including ethylene carbonate, hexene carbonate and octene carbonate could be synthesised from their corresponding epoxides and  $\text{CO}_2$  using Ce-La-Zr-O and HT-500 catalysts.

### **9.2.5. Continuous Flow Syntheses of Organic Carbonates**

Ce-La-Zr-O and HT-500 catalysts have shown remarkable catalytic activities for syntheses of cyclic carbonates from cycloaddition reaction of epoxide and  $\text{CO}_2$  using a high pressure batch reactor. It is important that performance of Ce-La-Zr-O and HT-500 catalysts should be investigate in

a continuous flow process in order to compare the efficiency of both processes for the synthesis of cyclic carbonate.

### **9.2.6. Economic Analysis of the Current Process**

This work has focused on the experimental and technical aspects of synthesis of industrially important chemicals using heterogeneous catalysts in the absence of any organic solvent. However, a comprehensive economic analysis and environmental benefits of the process could be compared to the conventional methods of cyclic carbonate synthesis that uses homogeneous catalysts in the presence of organic solvents. This would provide more insight on the potential advantages of the current method. Life cycle analysis (LCA) could be used as an important decision making tool to assess the environmental impact and economic feasibility of the process.

## ***CHAPTER 10***

## ***REFERENCES***

## 10. REFERENCES

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## ***CHAPTER 11***

## ***APPENDICES***

**11. APPENDICES****11.1. Appendix A: Unit Cell Parameters from La Bail fits**

<b>Sample ID</b>	<b>a</b>	<b>c</b>	<b>Volume</b>
<b>AP</b>	3.677 (0.001)	5.178 (0.001)	69.88 (0.02)
<b>HT-500</b>	3.666 (0.001)	5.200 (0.002)	69.88 (0.02)
<b>HT-700</b>	3.673 (0.001)	5.186 (0.001)	69.97 (0.02)
<b>HT-900</b>	3.681 (0.001)	5.179 (0.001)	70.17 (0.02)

**11.2. Appendix B: Data for Development of Calibration Curve****11.2.1. Data for Propylene Oxide (PO) and Propylene Carbonate (PC) Calibration Curve**

S/No.	Mass of PO (g)	Mass of PC (g)	Mass of Isooctane (g)
1	0.5222	0.1020	0.0624
2	0.4642	0.2041	0.0668
3	0.4062	0.3062	0.0712
4	0.3481	0.4083	0.0756
5	0.2901	0.5104	0.0700

**11.2.2. Data for Butylene oxide (BO) and Butylene Carbonate (BC) Calibration Curve**

S/No.	Mass of BO (g)	Mass of BC (g)	Mass of Isooctane (g)
1	0.1261	0.0346	0.5022
2	0.1198	0.0499	0.5054
3	0.1061	0.0674	0.5047
4	0.0869	0.0928	0.5067
5	0.0721	0.1219	0.5038
6	0.0685	0.1463	0.5077

**11.2.3. Data for 4-vinyl-1-cyclohexene 1,2-epoxide (VCHE) and 4-vinyl-1-cyclohexene Carbonate (VCHC) Calibration Curve**

S/No.	Mass of VCHE (g)	Mass of VCHC (g)	Mass of Isooctane (g)
1	1.1125	0.1114	0.1213
2	0.999	0.2224	0.1213
3	0.8618	0.3414	0.1238
4	0.7479	0.4564	0.1232
5	0.6257	0.5779	0.1202
6	0.4958	0.6848	0.1216

**11.2.4. Data for Epichlorohydrin (ECH) and (Chloromethyl)ethylene carbonate (CMEC) Calibration Curve**

<b>S/No.</b>	<b>Mass of ECH (g)</b>	<b>Mass of CMEC (g)</b>	<b>Mass of methanol (g)</b>
1	0.0832	0.0524	0.4287
2	0.0740	0.1248	0.4643
3	0.0647	0.1581	0.4415
4	0.0555	0.2647	0.4380

### 11.3. Appendix C: Publications

#### 11.3.1. Journal Papers

Adeleye, A. I., Patel, D., Niyogi, D., Saha, B. Efficient and greener synthesis of propylene carbonate from carbon dioxide and propylene oxide. *Industrial & Engineering Chemistry Research*, **2014**, 53(49), 18647-18657. (Full paper is attached to the thesis)

Adeleye, A. I., Kellici, S., Heil, T., Morgan, D., Vickers, M. Saha, B. Greener synthesis of propylene carbonate using graphene-inorganic nanocomposite catalysts. *Catalysis Today*, **2015**. <http://dx.doi.org/10.1016/j.cattod.2014.12.032>. Manuscript in press. (In press article is attached to the thesis)

Saada, R., Adeleye, A. I., Saha, B. Synthesis of dimethyl carbonate from carbon dioxide and methanol using heterogeneous catalysts. *Industrial & Engineering Chemistry Research*, **2015**. Manuscript submitted.

Adeleye, A. I., Saha, B. Utilisation of carbon dioxide for synthesis of vinylcyclohexene carbonate using heterogeneous catalyst. *Chemical Engineering Science*, **2015**. Manuscript submitted.

#### 11.3.2. Conferences Papers

Adeleye, A. I., Saha, B. Synthesis of propylene carbonate from carbon dioxide using novel heterogeneous catalyst. ChemEngDayUK, 7-8 April 2014, The University of Manchester, UK.

Adeleye, A. I., Patel, D., Saha, B. Utilisation of carbon dioxide using novel heterogeneous catalysts. Key note lecture delivered at the 21<sup>st</sup> International Congress of Chemical and Process Engineering CHISA, 23-27 August 2014, Prague, Czech Republic. (CD-ROM).



#### **11.4. Appendix D: Risk Assessment Forms**

The risk assessment forms for all the equipment and chemicals used in this research work are attached to the thesis.

### **11.5. Appendix E: LSBU Postgraduate key skills development training sessions**

- Conference Presentation – 18 June 2012.
- Academic Publications – 19 June 2012.
- Thesis Submission, Viva and Career Management – 20 June 2012.
- Key skills in the Research Environment – 05 November 2012.
- The student-Supervisor Relationship – 07 November 2012.
- Personal Effectiveness – 09 November 2012.

The certificates of attendance for the courses are attached to the thesis.